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LIQUID CRYSTALS

G. H. BROWN, J. W. DOANE, D. L. FISHEL AND V. NEFF

KENT, OHIO

AND

E. DRAUGLIS

BATTELLE MEMORIAL INSTITUTE

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FOREWORD

This report was prepared at Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201, under USAF Contract No. F33615-69-C-1001, Subcontract No. 70-8 (Ohio State University Research Foundation, Project No. 2731). The contract was initiated under Project 7340, Task 734001. It was administered under the direction of the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. T. E. Helminiak, AFML/LNP, as Project Scientist.

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This technical report has been reviewed and is approved.



R. L. VAN DEUSEN
Acting Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Liquid crystals are true liquids which have surface tension and the ability to flow and yet have some of the optical properties of crystals. Though these materials have been known for over eighty years, interest has been rekindled over the last ten years because of their many interesting technological applications. Modern research tools have provided much new basic information about the structure and properties of these materials. This basic information has been used to solve many technological problems and develop new devices. In classic fashion the successful application of known properties of liquid crystals has stimulated further basic research in the expectation of further practical exploitation of these unusual materials. Use of liquid crystals has been made in a wide variety of areas ranging from nondestructive testing by thermal mapping to display devices. Future applications of present day basic research will probably lie in the rheological properties, ordering properties and magneto-optical and electro-optical properties.

The present report is a brief state-of-the-art survey aimed at bringing the reader up to date on what is known of the fundamental properties of liquid crystals and their applications - potential as well as actual. The report is divided into three parts: a historical survey of the development of the science of liquid crystals, a summary of present knowledge of the physical and chemical properties of liquid crystals, and a section on present and possible future applications. Theories of the structure of liquid crystals, thermodynamics, the effect of external forces and fields, viscosity and diffusion, optical properties, and many other physical topics are discussed. Also covered in some detail are the

correlation of molecular structure with liquid crystallinity, synthesis of liquid crystals, and polymorphism. Applications discussed include non-destructive testing by means of color sensitivity, infrared and microwave detection, display devices, solvents for chemical reactions, and chromatography.

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PREFACE

The term "liquid crystal" is a seemingly contradictory term for a very interesting and unusual state of matter. The question that occurs to one upon meeting the phrase for the first time is "how can a crystal be liquid or how can a liquid be crystalline?" To counteract any possible confusion arising from the phrase "liquid crystal", several terms such as "mesomorphic state" or "anisotropic liquid" have been applied. However, ever since, O. Lehmann, the man who first correctly described the properties of this state of matter, coined the term, it has been in very wide use. The confusion arises from the fact that the molecules in a liquid are not arranged in any regular order that extends more than a few molecular diameters whereas the molecules in a crystal are fixed in regular three-dimensional lattices. In a liquid each molecule lies within a field of mutual attraction of its neighbors although it may sometimes wander out of this field entering the field of other more distant neighbors. In a solid there is no wandering of molecules; each molecule has a fixed position and cannot acquire sufficient energy to leave its original position unless the crystal is heated. When this is done thermal agitation tends to disturb the order so that when the temperature becomes high enough, the molecules escape from each other's influence and the solid melts—either to a liquid or a liquid crystal. The question then is what is liquid about liquid crystals and what is solid? In the next few paragraphs we shall attempt to answer this question in an elementary way and to describe the different types of liquid crystals known at present. It is hoped that this brief introduction will pave the way for a more fruitful reading of the main body of this report.

Liquid crystals may loosely be defined as substances that have some properties ordinarily thought to be characteristic of liquids and some properties ordinarily thought to be characteristic of solids. These materials cannot be

considered as rare; it has been estimated that one out of every 200 new compounds synthesized in the laboratory has liquid crystalline characteristics. Mechanically, liquid crystals resemble liquids, and have viscosities which range from that of runny glue to glassy solids. Some liquid crystals show unusual rheological properties in that the measured value of the viscosity is a strong function of the direction of flow of the substance. However, it is the optical properties of liquid crystals that most resemble those of crystalline solids. For example, some liquid crystalline substances scatter light in symmetrical patterns and the color of the reflected light is a function of the angle at which it is observed. Both their optical properties and the applications which they make possible are among the topics discussed in the body of this report.

Another way of looking at the difference between liquids, solids and liquid crystals is to consider the degrees of freedom of the molecules within the three states. In the liquid state the molecules are mobile in three directions and can rotate about three axes perpendicular to one another. In a crystal, the molecules are fixed and rotations are not possible. In liquid crystals, molecules are mobile in two directions and can rotate about one axis or are mobile in three directions and can rotate about one axis.

Liquid crystals are usually divided into three classes—smectic, nematic and cholesteric. In smectic liquid crystals, the molecules are arranged in layers with their long axes approximately normal to the plane of the layers. The molecules can move in two directions (in their own plane) and can rotate about one axis. The molecules within a layer may be regularly spaced as in a crystal or may be randomly distributed. The planes can slide easily over each other. (Figure 1) The term "smectic" comes from a Greek word meaning grease or slime and was applied to this type of liquid crystal because of its slippery feeling.

In nematic substances the only restriction on the arrangement of molecules is that they preserve a parallel or nearly parallel position with respect to each other. The molecules have mobility in three directions with rotation about one axis being permitted. This arrangement is analogous to a long box filled with round pencils which can roll around and slide back and forth, but remain parallel to one another in the direction of the long axis of the pencil. (Figure 2) The term nematic comes from a Greek word meaning thread and was applied to this type of liquid crystal because of the threadlike lines visible under microscopic observation.

In cholesteric materials the molecules are arranged in parallel layers about 2000 Angstroms thick, in contrast to smectic materials where the layer thickness is about the length of a molecule, about 20 angstroms. Each molecule in the cholesteric state essentially lies in a plane a few Angstroms thick. Very many such planes stack upon one another to form a several thousand Angstrom thick layer. Side chains project upward from the plane of each molecule and some hydrogen atoms extend below. Because of this the direction of the long axis of a molecule in a given plane is slightly and systematically rotated from the direction of the axis of the molecules in adjacent planes. The result is a helical structure which shows great optical activity because the layer distance of several thousand Angstroms corresponds to optical wavelengths. (Figure 3) The term cholesteric is applied to this class of liquid crystal because the first examples of it were derivatives of the substance, cholesterol. Cholesterol itself does not have liquid crystalline properties because it lacks the necessary side chains.

Liquid crystals have many odd and interesting physical properties which may be exploited to practical advantage. A striking example is given by the optical properties such as reflection, birefringence, circular dichroism, optical

rotation and color. These properties of a liquid crystal can all be very sensitive to changes in its environment such as temperature, pressure, presence of an electric or magnetic field or the presence of chemical vapors. The reason for this sensitivity is the weakness of the intermolecular forces responsible for the structure of the material. This weakness allows changes in the structure to occur under the influence of even very mild changes in environment. Perhaps, the most widely exploited optical property of liquid crystals is the color sensitivity of cholesteric liquid crystals. In the liquid phase these materials are colorless, but on cooling to the liquid crystalline phase or mesophase they go through a range of colors, appearing first violet, then blue, green, yellow, red and finally colorless again. The rate of change of color with temperature change varies from material to material. For a given material each color corresponds to an exact temperature. Hundreds of cholesteric materials, both pure and mixtures, are known and have been used to measure temperatures ranging from minus 20°C to 250°C. Further details of this application are to be found in the body of the report.

The remainder of this report is intended to bring the reader up to date on the current state of knowledge in liquid crystals. It consists of three parts: a historical background, a survey of the important physical and chemical properties of liquid crystals and the various interrelationships among them, and present and future applications.

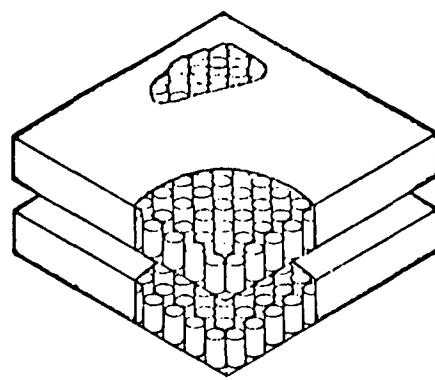


FIGURE 1. SMECTIC STRUCTURE

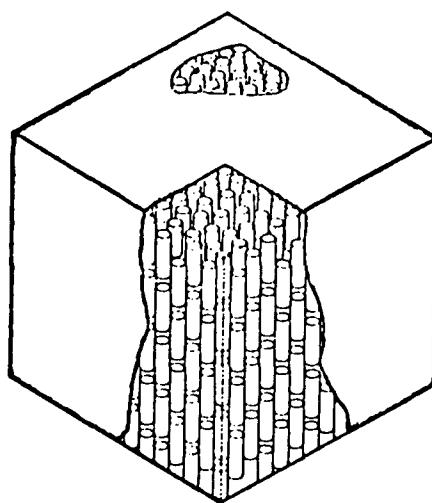


FIGURE 2. NEMATIC STRUCTURE

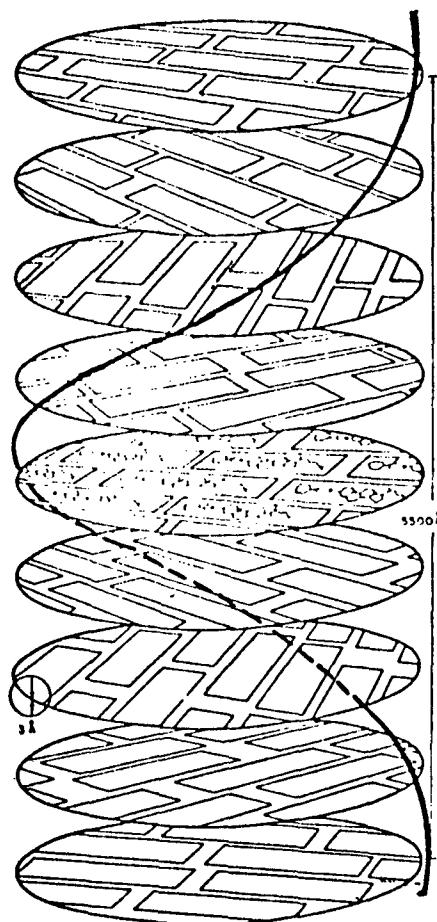


FIGURE 3. CHOLESTERIC STRUCTURE

I. HISTORY OF LIQUID CRYSTALS

A. EARLY WORK IN THE FIELD

Friedrich Reinitzer¹⁹ is credited with the discovery of liquid crystals. He prepared cholesteryl benzoate and briefly sketched its properties. However, the properties of liquid crystallinity were correctly described by Lehmann¹⁵, who explained that the liquid crystalline state shows turbidity. On studying cholesteryl benzoate he found that in the liquid crystalline state the material flowed like "oil" and that it changed color with change in temperature. Lehmann was the first to suggest the name liquid crystals for those substances which are liquid in their mobility and crystalline in their optical properties.

A rather exhaustive list of articles found in the early literature¹⁻²⁷ may be found at the end of this report. The early literature probes primarily the optical properties of liquid crystals²⁸⁻³⁶, their flow properties, theory of their structure³⁷⁻⁴¹, and the discovery of new compounds. Leaders in these early studies include Lehmann, Schenck and Reinitzer with Lehmann²⁸⁻³⁶ being the most productive and the most careful in his research on this interesting state of matter. Some of his descriptions of liquid crystals have stood the test of time and some of his books are classics in the field. His major contributions are definitions of the optical properties of liquid crystals. It was in this early period that Bose³⁷⁻⁴¹ proposed the swarm theory to explain the structure of liquid crystals. This theory was the predominant one for approximately fifty years.

Liquid crystals did not take the fancy of many scientists during the period from their discovery through the first two decades of the 1900's.

B. AN ACTIVE PERIOD IN THE 1920'S AND 1930'S

The first serious study of liquid crystals by scientists representing a variety of disciplines took place over a period of about ten years from

the early 1920's through the mid 1930's. Some outstanding scientists made significant contributions to the field. These include Kast, Friedel, Lawrence, Bernal, Vorlander, Gaubert, C. Hermann, Ornstein, Oseen and Zocher. Some of these persons still maintain an active interest in the field. In the interval between 1900 and 1920 there were a few interesting observations recorded in the literature, the most important being the discovery of layer packing of certain liquid crystalline systems. This layer packing is now known as Grandjean terraces.

Research in the 1920's and 1930's resulted in some outstanding observations of the properties and structure of liquid crystals, including both lyotropic and thermotropic systems. The major contributions may be catalogued as follows:

1. Friedel⁴² assigned names to the classes of liquid crystals based on their optical properties. He identified the nematic and smectic classes and first proposed that the cholesteric class was a special kind of nematic structure.
2. Zocher⁴³ introduced the concept of the continuum theory. This theory did not have much support during its earlier years but has come into prominence within the past five years.
3. Kast and Ornstein⁴⁴ expanded the swarm theory which explained many of the optical, electric and magnetic properties of nematic liquid crystals.
4. Lawrence⁴⁵ and Jelley⁴⁶ distinguished between lyotropic and thermotropic liquid crystals, especially on the methods of their preparation and some of the similarities the two types possess.
5. Hermann⁴⁷ classified matter into twenty translation types from amorphous to crystalline. This classification with proposed X-ray diffraction patterns⁴⁸ has afforded some guidance to scientists working on the structure of mesomorphic materials.

6. Bernal and his coworkers⁴⁹ did some X-ray studies of crystals of compounds which became liquid crystals on heating. These studies, although introductory, still represent a part of the scanty structural data available.
7. Bernal made some interesting observations on the role of liquid crystals in living systems. Bernal and Fankuchen^{51,52} showed that tobacco mosaic virus with water forms liquid crystalline systems.
8. Dielectric properties were studied extensively during this period. Some of the outstanding work was done by Kast⁵³. This work was expanded later, especially by Maier.
9. Synthesis of new thermotropic liquid crystals became fashionable in this period. Vorlander⁵⁴⁻⁵⁹ and Gaubert⁶⁰⁻⁶⁵ were the most productive. Most of the research was on Schiff's base type of compounds.
10. Bragg⁶⁶ made a valuable contribution to the structure of the smectic state. He carefully explained the stratification in their structure.
11. It was in this period that the first data were taken on viscosity, surface tension, refractive index, optical rotation and magnetic susceptibility.

C. THE RENAISSANCE OF LIQUID CRYSTALS

After the European Conference in 1931 (recorded in Transactions of the Faraday Society, 1933), research in the field of liquid crystals almost disappeared from the scene. There are at least two reasons for this retrenchment. It seems that researchers who met for the European Conference in 1931 had extended their studies as far as possible with the instrumentation available. Also, the period leading up to and during World War II found many scientists pulled away from their chosen research interests and assigned to research for the war effort.

The first industrial product which took advantage of liquid crystallinity was manufactured during this period. Polacoat, Inc. was founded in 1946 after its founder learned how to make a light polarizer using a manufacturing process that took advantage of liquid crystalline properties.

During the 1930's and 1940's lyotropic liquid crystals were being studied with considerable interest. Vold⁶⁷⁻⁷⁰ and his co-workers were studying the properties of soap solutions and were beginning to develop classifications of the different textures.

The dormant field got its first shot in the arm with the appearance of a review of the field written by Brown and Shaw⁴⁸. Research from 1957 until about 1965 was carried on by a small but increasing number of scientists. Maier and Saupe^{71,72} developed a statistical theory of the nematic phase in the earlier part of this period. This theory continues to be considered an outstanding contribution to the field. Optical properties, field effects, light scattering and other physical properties were being studied by a few scientists in the late 1950's and early 1960's.

In 1965 the First International Liquid Crystal Conference was held at Kent State University (August 16-25). This conference was the catalyst which the field needed. It evolved out of research which had been in progress for several years. The papers presented at that conference showed a continuing interest in synthesis of new liquid crystalline compounds, a comparison of properties of members of homologous series and a study of the influence of substituents on properties of liquid crystals. Optical studies of smectic, nematic and cholesteric textures continued to be a center of interest and instrumentation for these studies was greatly improved over that available in earlier work. In the mid 1960's there was a new sense of direction in research on liquid crystals with more concentration on molecular properties than on bulk properties. It was in this period that Saupe and Englert published their first nuclear magnetic resonance studies using nematic liquid crystals as solvents. This research opened up new avenues for those interested in NMR. Some very exciting findings have resulted from these studies, including structure determination of solutes dissolved in nematic liquid crystals.

During the 1965 conference it was agreed that a second conference would be held in 1968. The conference was held at Kent State University, August 12-16, 1968. The number of attendees and the number of papers presented was more than twice, in both cases, the number in 1965.

Research activity in liquid crystals took on a new dimension from 1965 to the present. The papers presented at the 1968 conference covered a large spectrum of subjects. A brief synopsis of the papers presented at the conference will suffice to give the reader a sense of the growth of the field. The three plenary lectures covered the general subjects of lyotropic liquid crystals, the correlation of molecular structure and the physical properties of thermotropic liquid crystals and liquid crystals in living systems. The six conference lectures focused on "the state of the art" in a variety of areas. These include block copolymers as liquid crystalline structures, a review of synthetic work in the field over the past several years, the thermodynamics of phase transitions, the role of liquid crystals as solvents in nuclear magnetic resonance and the continuum theory as an explanation of the structure of nematic liquid crystals.

Contributed papers showed more concentration on molecular properties than on bulk physical properties. There was still an interest in the synthesis of new compounds which may exhibit unusual properties such as response to external influences (e.g. electric and/or magnetic field). Study of optical properties of liquid crystalline substances remained very popular and experimental techniques such as nuclear magnetic resonance (NMR) and infrared which measure directly parameters associated with individual molecules are gaining a wider audience. The experimental techniques used to study structure were quite varied and included X-ray, nuclear magnetic resonance, spin resonance, ultrasonics, optical microscopy, electron microscopy of lyotropic systems, and electrical and magnetic field effects on optical properties. The continuum theory, a model for molecular arrangement in liquid crystals, was the most popular of the approaches to an explanation of the structure of nematic liquid crystals. The swarm theory, which for many years afforded the most popular explanation of the properties of the nematic structure, had little support among those who attended the 1968 conference.

Multi-component liquid crystalline systems (e.g. lipid-water systems) received considerable attention with about 25 percent of the papers covering this field, including liquid crystals in living systems. In systems of inanimate materials the most popular lyotropic systems were lipids and water, surface-active agents and water and poly- ν -benzyl-L-glutamate in water. Liquid crystals in living systems got more attention at this conference than at prior conferences. Change of phase and change of state in living systems were given consideration as well as the role of liquid crystals in cellular membranes and in muscle fibers.

Within the past ten years the different kinds of lyotropic liquid crystals have been classified from their X-ray diffraction patterns⁷³. Within the past two years much progress has been made in classifying thermotropic liquid crystals from their X-ray diffraction patterns. At least five smectic textures have been characterized from X-ray data⁷⁴.

Sackmann and Demus⁷⁴ have clarified the status of smectic textures by use of microscopic techniques and X-ray diffraction. From X-ray patterns they have found that smectic textures have a sharp interference at a small angle (less than 2 degrees, Bragg angle) which corresponds to the spacing between strata of molecules. At larger angles the different smectic textures show different interference patterns. The texture classified as smectic A shows a broad peak at about 10 degrees (Bragg angle) which indicates that the molecules within a stratum possess an essentially random distribution. The smectic B texture has a sharp peak in the X-ray diffraction pattern at 10 degrees indicating that there is much more order in the arrangement of molecules in a stratum than is found in smectic A. The profile of the peak at 10 degrees for a smectic C modification indicates that the intermolecular arrangement has more order than in smectic A but less order than in smectic B. Smectic D is found to be isotropic while smectic E gives a rather unusual X-ray diffraction pattern. In addition to the sharp peak at low angles which is characteristic of smectics A, B, and C there are three peaks at 9.6 degrees, 10.9 degrees and 13.5 degrees. This information indicates that there is a high degree of order within strata in smectic E.

Since 1965 research and interest in liquid crystals has been increasing very rapidly. Most major companies in the United States have research projects on the subject. More and more academic people are getting interested in the field. Research groups requesting lectures on liquid crystals have increased by leaps and bounds in recent years.

With the great interest in liquid crystal research one would expect the development of applications. The use of cholesteric liquid crystals as temperature sensors is well established. Liquid crystals, especially nematic ones, are being used in display systems. Their use to make light polarizers was first developed in the 1940's. The role of liquid crystals in living systems is just beginning to be explored. Potential new applications are large in number and as our knowledge of the structure and properties of liquid crystals expands applications will multiply.

II. THE PHYSICS AND CHEMISTRY OF LIQUID CRYSTALS

A. THEORIES OF THE STRUCTURE OF MESOMORPHIC PHASES

It is not a simple matter to define a mesomorphic phase. Historically the three common types of mesophase--nematic, cholesteric, and smectic--were described and characterized almost exclusively by optical methods. The characteristic nemas or threads of the nematic phase, the brilliant irridescence of the cholesteric phase, and the Dupin cyclides and focal conics of the smectic phase. These are rather objective descriptions based on direct observations of specific physical quantities and, although they are correct, there exists the need for a somewhat broader perhaps more subjective description, in order to get things in perspective and to make possible communication on common ground. This problem of proper definition of a liquid crystal has become particularly acute in recent times because many examples of polymorphism, particularly in the smectic phase, have been reported. Sackmann and Demus^{1,2} have given the most attention to the classification of different smectic structures. Leclercq et. al.³ have reported the strange result of two cholesteric type structures separated by a definite first order phase transition. In a very recent paper, based on the analysis of general angular force fields, Freiser⁴ has suggested the possibility of a second type of nematic phase which would be optically biaxial. These observations, which may not all be correct or correctly interpreted, are hard to understand on the basis of classical definitions of liquid crystal structure.

The one underlying feature common to all types of mesophase is the presence of long range order. The order may be associated with the translational or rotational degrees of freedom of the liquid. One manifestation of the long range order is the general observation of anisotropy in many physical properties. This, in turn, is what makes liquid crystals interesting from the point of view of applications and new devices. It is possible to think of the state of matter called liquid crystal in a very broad way. We might classify all fluid substances which have long range order and which lie in the range between the perfectly translationally and

rotationally ordered crystal and the perfectly isotropic liquid as the class of liquid crystals. From this point of view the class of liquid crystals is very broad indeed. The proper classification scheme for liquid crystals becomes then a very large generalization of the field of crystallography as has been pointed out by Zocher⁵. What strikes the imagination about this way of looking at liquid crystals is not so much the types of structures that are known as the vast possibilities for structures which have not yet been observed or classified. There are certainly limitations to be imposed on the possibilities of long range order in three dimensions. However, these restrictions and limitations are not well understood. The theoretical study of the types of long range order that are possible, given the rich variety of types of intermolecular forces, has barely begun. It is unlikely, for example, that one could have long range translational order involving two translational degrees of freedom (the smectic phase is characterized by translational long range order in one degree of freedom). It is probably also unlikely that one could have a one-dimensional liquid crystal. Studies of the thermodynamic limitations for ordinary crystals were initiated long ago by Landau⁶. Much more of this type of work needs to be done and would be of immense value in attempts to classify liquid crystals and to prepare new and different types of structures.

There has been much confusion in the past concerning the factors which give rise to liquid crystallinity and the actual structure of different mesophases. The reason for confusion is not difficult to perceive. Any realistic theory of liquid crystal structure has to account for the remarkably diverse and subtle changes in physical and optical properties brought about by surfaces and weak external forces. Therefore one must be consistently on guard against a superficial or cavalier approach to this subject. In the following paragraphs, we shall review the theories of liquid crystal structure beginning with the nematic phase.

1. The Swarm Theory of Nematic Liquid Crystals

The swarm theory was proposed originally by Bose⁷ and was taken up and promoted most vigorously by Ornstein and Kast⁸⁻¹⁰. The observations

which led most directly to the swarm concept were those of light scattering and the effects of weak electric and magnetic fields. A swarm was supposed to be composed of clusters of molecules with definite boundaries. Such a cluster was thought to contain from 10^4 to 10^6 molecules¹⁰ arranged approximately parallel so that a unique axis could be defined for the swarm. The direction of the swarm axes, however, was assumed to undergo random thermal fluctuations and the boundaries of the swarm were not held to be fixed in time, but to change according to molecular diffusion and Brownian motion. This latter process of change of swarm morphology in time, however, has never been described in detail. The appeal of the swarm concept was related to the fact that one could postulate large values for additive properties such as electric polarization or magnetic susceptibility associated with a swarm. One could then easily employ a statistical theory similar to that of Langevin to determine such things as size and moment of inertia of a swarm, saturation effects due to external fields, etc. Experimentally determined values for these quantities have been reported by many investigators¹¹. We must point out here, however, that these values are largely meaningless because the swarm concept as originally defined by Kast is not a correct description of the structure of the nematic phase.

The swarm theory has been severely criticized, originally by Zocher^{12,13}, who recognized that the physical properties of liquid crystals, particularly those pertaining to the effects of external forces and orienting surfaces, could be explained by an extension of the concepts of continuum mechanics. This viewpoint is now known as the continuum theory of liquid crystals. A kind of confused conflict has grown around the swarm theory versus the continuum theory of liquid crystals. Much of the confusion is based on misinterpretation and a few general comments will be made here in order to attempt to alleviate the confusion. The basic feature of the swarm theory is that a microscopic entity (a swarm) is defined with a unique axis (that of parallel orientation). As mentioned previously, the direction of the swarm axes, in the absence of external forces or orientating surfaces, i.e. in the bulk of the liquid, would be subject to randomization due to thermal fluctuations. Hence, in the absence of external forces, physical properties would be isotropic in the bulk of the liquid and would become

anisotropic only in regions very close to orienting surfaces. This expectation, however, is now well known not to be true. A nematic liquid crystal is uniformly oriented throughout the bulk of the liquid except at singularities produced by foreign objects or impurities. This fact was most clearly demonstrated in the pioneering work of Frederickz and Zolina¹⁴. Now, as we shall see, the continuum theory can explain these results and all others because weak elastic moduli which are masked in solids become prominent in liquid crystals and lead to a clear interpretation of their properties including the long range order. It must be understood that the conflict between the swarm theory and the continuum theory is not to be interpreted as a triumph of continuum mechanics over a molecular approach to the problem. A valid molecular approach should agree with and reinforce the continuum theory. However, a correct and comprehensive molecular theory of the nematic phase based on statistical mechanics is yet to be achieved. The concept of swarms (not to be confused with cybotactic groups which might be very much smaller and could well be present in liquid crystals as a result of short range order) is simply incorrect.

2. The Continuum Theory

The continuum theory applies to all types of mesophase. It was proposed by Zocher and treated more mathematically (and also in a more confused way) by Oseen¹⁵. This is really an important generalization of elasticity theory to include anisotropic liquids. A liquid crystal is assumed to be liquid in the sense that a shear stress is not opposed by permanent static forces. A new type of deformation, however, not involving a change in distance between small regions of volume, is defined. This type of deformation is called a curvature "strain" and can be induced by a torque "stress". Frank¹⁶ has given the clearest formulation of this theory of curvature deformation. These ideas have been generalized recently particularly in the important series of papers by Ericksen¹⁷⁻²⁰. It must be kept in mind, of course, that this approach to liquid crystal structure is strictly phenomenological. The theory has nothing to say about what types of molecules or intermolecular forces will give rise to mesophase structures.

In the theory of elastic deformations of a solid body the energy density is expanded into a quadratic form in the deformations or elastic strains. A similar expansion is postulated for the continuum theory of liquid crystals except that the deformation coordinates are curvatures rather than the usual displacements. The curvature coordinates are defined on a vector \mathbf{N} which is called the director. This vector is tangent, at each point of the liquid, to lines tracing out the direction of parallel molecular orientation. In the hydrostatic theory the vector field of the director, including its values on surface boundaries, completely defines the state of deformation in a homogeneous region. The curvature coordinates are the components of the tensor gradient $\nabla \mathbf{N}$ of the director. The magnitude of the director has no obvious physical significance so it is taken as a unit vector. If we choose a coordinate system in which the z axis is along \mathbf{N} , the elements of the gradient tensor are as follows:

$$\begin{pmatrix} \frac{\partial N_x}{\partial x} & \frac{\partial N_x}{\partial y} & \frac{\partial N_x}{\partial z} \\ \frac{\partial N_y}{\partial x} & \frac{\partial N_y}{\partial y} & \frac{\partial N_y}{\partial z} \\ 0 & 0 & 0 \end{pmatrix}$$

In the notation of Frank these curvature coordinates are defined as

$$\begin{array}{lll} s_1 = \frac{\partial N_x}{\partial x} & t_1 = -\frac{\partial N_y}{\partial x} & b_1 = \frac{\partial N_z}{\partial z} \\ s_2 = \frac{\partial N_y}{\partial y} & t_2 = \frac{\partial N_x}{\partial y} & b_2 = \frac{\partial N_y}{\partial z} \end{array}$$

splay twist bend

From the definition of the curvature "strains" it is seen that the theory is intrinsically non-linear. The total free energy of the liquid crystal is expressed as the volume integral

$$G = \int_V U \, dV$$

and it is assumed that \underline{U} can be obtained by an expansion in powers of the gradient tensor $\nabla \underline{N}^{21}$. Retaining only second order terms one can express \underline{U} as

$$U = \text{Tr } (K) (\nabla \underline{N} - \nabla \underline{N}^0)^2$$

where K is a 9X9 matrix of proper derivatives of \underline{U} defining the "elastic constants", and $\nabla \underline{N}^0$ is a constant matrix which takes account of the fact that the state of lowest energy may not be that for which $\nabla \underline{N} = 0$. That is, a state of uniform curvature may be the state of lowest energy (e.g. cholesteric liquids). The inherent symmetry of liquid crystals leads to a tremendous simplification of the matrix of elastic constants. The various symmetry conditions and constraints on N have been discussed by Frank¹⁶ and more recently by Ericksen¹⁷⁻¹⁹. We will consider first the nematic and cholesteric structures because they are very closely related. The hydrostatic theory of the smectic phase requires special consideration.

3. Nematic and Cholesteric Structures

A perfectly isotropic liquid is characterized by complete lack of order with respect to translation and rotation. That is, the system has the symmetry of the full group O_3XT_3 . In a nematic or cholesteric liquid crystal the translational symmetry is retained but the rotational symmetry is broken from O_3 to O_2 . That is, there is cylindrical rather than spherical orientation symmetry. The O_2 symmetry can be used to reduce the number of non-zero constants in the matrix of elastic constants from forty-two to seven. The actual expression for the energy density can be found in Frank¹⁶. If one assumes that there is also no intrinsic polarity in the liquid, that is, the energy density is invariant under $\underline{N} \rightarrow -\underline{N}$, two additional constants can be eliminated. The resulting expression can be written as

$$2U = k_{11}(\nabla \cdot \underline{N})^2 + k_{22}(\underline{N} \cdot \nabla \times \underline{N} + t_0)^2 + k_{33}[(\underline{N} \cdot \nabla) \underline{N} \cdot (\underline{N} \cdot \nabla) \underline{N}]$$

where the term t_0 , in Frank's notation, refers to a uniform constant twist and k_{11} , k_{22} , k_{33} are the constants for splay, twist, and bend originally defined by Zocher¹². The energy density expression with these constraints is postulated to be that for the cholesteric phase. Hence in the minimum energy configuration the cholesteric phase is characterized by a uniform twist. The twist is presumed to arise because of enantiomorphy. That is, all known cholesteric liquid crystals consist of optically active molecules. The vector \mathbf{N} is uniform (nematic) in each of a family of parallel planes and twists continuously about the normal to these planes. This model of the cholesteric structure is identical to that used by de Vries²¹ in his theory of the optical properties of cholesteric liquid crystals. It has been pointed out by de Gennes²² that spiral structures can be expected, in principle, in a medium in which the molecules are not optically active. In this case the energy density would have a double minimum; the two minima are equally displaced from $\nabla \mathbf{N} = 0$. In this case one might expect a random growth of right or left spiral patterns. These structures, however, have never been observed in liquid crystals.

If t_0 is equal to zero we have the expression for the energy density of the nematic structure. Hence, from the point of view of the continuum theory, the nematic structure is just an untwisted cholesteric structure. The conditions for the nematic structure, as stated by Ericksen, are the general symmetry principles stated above plus the condition that $\nabla \mathbf{N} = 0$ is the state of lowest energy. Hence for the nematic phase we are left with only three independent constants for twist, splay and bend. Saupe has reported approximate values for the curvature elastic constants for a nematic liquid²³. Their magnitude is of the order of 10^{-6} dynes but they are not equal and show a large temperature dependence. It should be noted that the elastic constants for a liquid crystal are very much smaller than the ordinary elastic constants for a solid (about sixteen orders of magnitude). This point has been emphasized in a recent discussion by Zocher²⁴. Hence, the smallest perturbations due to impurities, foreign particles, surface inhomogeneities, or weak external forces, can have a severe and long range effect on the structure of liquid crystals. Because of this, on optical examination of a liquid crystal sample, one rarely sees the idealized

unperturbed equilibrium configuration. Many different types of structural perturbations and singularities have been observed in the nematic and cholesteric phase. One prominent example would be the threads or nemas in nematic liquids from which they take their name. Some types of singularities in nematic liquids were discussed by Frank¹⁶ and called by him disinclinations. These are predicted from the continuum theory (under certain simplifying assumptions) and are essentially the singular solutions of the Laplace equation in two dimensions. Some of these types of disinclinations in liquid crystals have been observed experimentally but it must be pointed out that many singularities and distortions observed in liquid crystals have not been explained by any theory, especially those induced by external electric or magnetic fields. Another important type of disinclination observed often in cholesteric liquid crystals was described first by Grandjean²⁵ and has been called a Grandjean plane. These optical patterns are observed only if the cholesteric liquid is confined in a wedge-shaped space provided by slightly tilted glass or mica plates. They appear as bright stripes parallel to lines of equal thickness along the glass surface. Since the distance between the stripes is highly dependent on the thickness and wedge angle it seems that such a system might be used as a very sensitive pressure gauge although no practical application of this phenomenon has been made up to this time. It is now known that the Grandjean planes are not "planes" but lines. A sound and reasonable theory of these line singularities has been proposed by Cano²⁶ and has been recently confirmed in the convincing experiments of Kassubeck and Meier²⁷. They have also been discussed theoretically (although not particularly clearly) from the point of view of the continuum theory by de Gennes²². The Orsay liquid crystal group has reported the observation of a new type of double disinclination line in high pitch cholesteric compounds²⁸. These lines presumably give rise to a discontinuous jump of two half pitches. Again this phenomenon is worth investigating from the point of view of some practical application. They break into a zigzag pattern in the presence of a sufficiently high magnetic field. Friedel and Kleman²⁹ have suggested a structural model for this phenomenon.

The structural properties of liquid crystals discussed so far have been based on the hydrostatic continuum theory. It should be pointed out that some aspects of the hydrodynamic behavior of nematic and cholesteric liquids have been considered recently by several investigators^{23,30-34}. These are based primarily on the work of Ericksen and have been extended by Leslie³⁵⁻³⁷, Coleman³⁸ and Wang³⁹. The current status of the theory is discussed in Ericksen³³. The major emphasis has been of viscosity and the propagation of various types of orientation waves. Earlier references to viscosity measurements can be found in Gray⁴⁰ or Brown and Shaw¹¹. One topic of interest is the size effect in viscosity measurements where orientation induced by capillary walls can compete with orientation induced by shear flow. This effect is discussed by Leslie⁴¹ and Ericksen²⁰ and compared with the experimental results of Porter and Johnson⁴² and Porter, Barrall and Johnson⁴³.

4. The Smectic Phase

As mentioned previously, the continuum theory of the smectic phase requires separate considerations. This is due to the breaking of the continuous translational symmetry in one dimension. That is, there is one dimensional translational order. The classification of the smectic phase due originally to Friedel⁴⁴ requires that molecules be arranged parallel in layers with the molecular axes normal to the layer. The geometry imposed by the layers, which may be curved surfaces, leads naturally to the explanation of the optically characteristic Dupin cyclides and focal conics¹¹. In terms of the continuum theory the splay constant should be very large (solid like) so that the twist and bend deformations can be neglected in comparison according to Oseen¹⁵ and Frank¹⁶. The details of the elastic constants for the smectic phase have been discussed by Saupe⁴⁵. The structural description of the smectic phase on the basis of the continuum theory is complicated by the fact that there is considerable polymorphism in this type of mesomorph. A detailed discussion of polymorphism in the smectic phase and the experimental characterization of different types of smectic structure has been given by Sackmann and Demus⁴⁶ (see Part I). Also, some recent examples of polymorphism have been reported by Fergason et. al.⁴⁷⁻⁴⁹. Some of the

types of smectic structure which might be expected on the basis of continuum theory have been discussed in an important paper by Saupe⁴⁵. These include a tilted smectic structure, a twisted type structure, a smectic with a double layer structure, and a ferroelectric layer structure.

Finally, we mention an interesting material, discussed by Saupe⁴⁵ and first described by Lehman⁵⁰. This is a presumably metastable liquid crystal obtained from a cholesteric compound such as p-n-nonylphenyl carbonate by cooling rapidly from the isotropic phase. The liquid is optically isotropic in the undeformed state. It becomes double refractive when exposed to slight mechanical stress or surface distortion.

B. THE EFFECT OF EXTERNAL FORCES AND FIELDS

The structural state of a liquid crystal is very sensitive to external forces as well as boundary conditions at surfaces. Many external stimuli are known to affect the physical and optical properties. These are static and alternating electric fields, static and rotating magnetic fields, mechanical forces and torques, ultrasonic fields, even a moderately intense electromagnetic field as has been shown recently by Saupe⁵¹. A large amount of work has been reported in this area recently but it cannot be said that there is general agreement on the interpretation of results. We shall discuss the effects of external forces separately for the three different types of thermotropic liquid crystals.

1. Nematic Materials

An effect of primary importance in nematic liquid crystals is the alignment produced by a static electric or magnetic field. Fields which are far too weak to produce a torque sufficient to align single molecules at the temperature of the liquid crystal phase are strong enough, however, to affect the weak elastic constants described in the continuum theory. In the case of a magnetic field, the coupling to the director occurs through the anisotropy of the molecular susceptibility associated primarily with the

pi electrons of the characteristically aromatic molecules. This requires an additional energy term to be added to the free energy density involving the dot product of the field strength with the vector field of the director. These effects have been discussed by Saupe²³, de Gennes²² and Pincus et. al⁵².

There have been a large number of investigations of the effects of electric and magnetic fields on the structure and morphology of liquid crystals. The field dependence of the magnetic susceptibility of the liquid crystal phase of p-azoxyanisole has been studied recently by Masson and Poulis⁵³. A similar study of the effects of a homogeneous electric field has been reported by Neff, Gulrich and Brown⁵⁴. The theoretical interpretation of these effects is, however, incorrect, since it is based on swarm theory. The dielectric anisotropy of several nematic liquid crystals has been studied in a series of papers by Maier and Meier⁵⁵⁻⁵⁷. The dielectric dispersion over a range of frequencies has been studied by Maier and Saupe⁵⁸ and by Axeman et. al.⁵⁹⁻⁶¹. In these experiments the nematic liquid crystals are oriented by a magnetic field. The normal Debye dispersion is found at microwave frequencies but the azoxy compounds, which have the largest principal value of the dielectric tensor perpendicular to the molecular axis show an additional dispersion of the parallel component at very low frequencies in the radio range. This is a surprising anomalous behavior and is intimately related to the structure of the nematic phase. It has been discussed theoretically by Maier and Saupe⁵⁸. Carr et. al. have made an extensive study of molecular ordering due to electric and magnetic fields⁶²⁻⁶⁹. Their procedure is to study the dielectric loss of a relatively thick sample (1 mm) by means of microwaves at a fixed frequency. An external magnetic or alternating electric field can be applied simultaneously. Some interesting results have been obtained that are not fully understood. For example, compounds with negative dielectric anisotropy, such as p-azoxyanisole, are aligned parallel to a d.c. or low frequency electric field but they are aligned perpendicular to a high frequency (300 kHz) electric field. In general the effects of electric fields are not as well understood as magnetic fields. There are difficult problems associated with streaming due to the motion of ionizable impurities etc.

A great variety of interesting optical effects have been observed with electric and magnetic fields. Williams⁷⁰ and Kapustin and Vistin⁷¹ were the first to report a typical pattern observed in nematics in a weak electric field. This mosaic pattern has been called a domain structure and there is much confusion in the literature concerning the interpretation of this structure. It can also be produced by a magnetic field or by ultrasonic excitation. A threshold voltage is required to produce the domain pattern which is typically 500-700 V/cm and is dependent of frequency, temperature, and film thickness. Williams^{70,72,73} and Williams and Heilmeier^{74,75} have done a variety of experiments in order to understand the nature of domain formation. The best approach to a theory of these effects with electric fields has been reported recently by Meyer⁷⁶. Domain formation with magnetic fields has been discussed theoretically by Helfrich⁷⁷. Another effect called dynamic scattering has been reported recently by Heilmeier^{78,79}. This has been observed with the nematic compound anisylidene p-aminophenylacetate. A thin film, which is initially transparent, scatters light strongly (appears white) when subjected to d.c. fields of 5×10^3 V/cm. This should not be confused with domain formation which is achieved with fields which are an order of magnitude less intense. The explanation given by the authors is based on the formation of scattering centers by the transport of ions through the ordered medium. Heilmeier and Zononi⁸⁰ have also used electric fields to orient dye molecules dissolved in a nematic liquid. They have been able to color switch samples with an electric field. These field effects have obvious potential for device applications and will be discussed further in Part III.

2. Cholesteric Materials

Studies of the effects of electric and magnetic fields on cholesteric compounds are comparatively recent. The structure of the cholesteric phase is characterized by a uniform twist in the absence of external forces. This twisted structure gives rise to unusual optical effects which can be explained by a selective Bragg reflection determined by the pitch of the helix. Also, the phase is characterized by extremely large optical rotations. These optical

effects were first explained by de Vries²¹ and have been studied by Fergason et. al.^{81,82} The wavelength of the reflected light is very temperature sensitive. The temperature variation of the pitch is not well understood, although an interesting explanation has been given recently by Keating⁸³. This is based on the presence of anharmonicity in the forces resisting the relative twist of neighboring planes of molecules and views the macroscopic twist as the rotational analog of thermal expansion in a solid.

According to the continuum theory, the cholesteric structure is just a twisted nematic structure due to enantiomorphy. One might then ask whether the cholesteric structure can be untwisted by an electric field or by mechanical forces. In the case of a magnetic field this problem has been considered theoretically by de Gennes⁸⁴. He finds that a very large field would be required to untwist a pure cholesteric compound (ca. 100 kG). The actual untwisting has been observed, however, for a mixture of cholesteric and nematic compounds with a large pitch. This observation has been reported by Durand et. al.⁸⁵. The experimental results are in excellent agreement with de Gennes' theory. The first observations of the untwisting of the cholesteric structure were reported by Sackmann, Meiboom and Snyder⁸⁶. The significance of these results is the fact that one can apparently obtain the twisted structure with optically active nematic compounds. A series of such compounds have also been prepared by Leclercq et. al.³. These authors report transition temperatures and heats of transition and find, in some cases, two cholesteric structures separated by a definite first order phase transition. This result is difficult to explain on the basis of the accepted concept of the cholesteric structure as a twisted nematic. There is need for much further study concerning the proper characterization of a phase, especially in view of the variety of transitions which have been observed recently.

The structure of mixtures of cholesteric esters has been studied by Sackmann et. al.⁸⁷ and by Haas and Wysocki⁸⁸. The pitch of the helix can be varied by changing the composition of the mixture. The change in pitch with composition is not well understood and no suitable theory has been proposed to explain it. Adams et. al.⁸⁹ have studied reflection from cholesteric films subjected to mechanical disturbance. The scattering characteristics of the undisturbed and disturbed materials are quite different

and it is possible, by simply dragging a cover slide over the surface, to bring about a reorientation of the optic axis from a direction initially in the plane of the supporting surface to direction perpendicular to it.

Optical studies of the effect of electric fields on cholesteric films have also been reported⁹⁰⁻⁹². A variety of complicated optical features are observed such as spots and Maltese crosses, but they are not well understood. The domain patterns characteristic of nematics are not observed. Wysocki et. al.^{93,94} have reported what they call a phase change in cholesteric liquid crystals in a strong d.c. electric field (ca. 10^5 V/cm). The change is from optically negative to positive birefringence and has been interpreted as a transition from the cholesteric to the nematic phase caused again by the untwisting of the cholesteric structure.

3. Smectic Materials

There has been no extensive work on the effects of electric or magnetic fields on the structure of the smectic phase. In general weak fields have little effect on the physical or optical properties. This is not surprising because of the greater magnitude of the elastic deformation constants associated with the one dimensional crystalline order in these materials. The formation of a domain pattern in a strong electric field has been reported by Vistin and Kapustin⁹⁵.

C. THERMODYNAMICS OF THERMOTROPIC LIQUID CRYSTALS

In comparison with the vast amount of information on the thermodynamic properties on solids and isotropic liquids, the number of significant thermodynamic studies on liquid crystals is extremely small. There is a real need for equation of state data and phase diagram studies on single component thermotropic liquid crystals.

1. Statistical Theory of Phase Transitions

Liquid crystal phase transitions are typically first order with latent heats of 0.1-0.7 kcal/mole (nematics and cholesterics) and 1-3 kcal/mole (smectics). The volume changes for the isotropic-nematic transition are also small, generally about one order of magnitude smaller than comparable liquid-solid transitions. As mentioned previously, a statistical theory of the nematic phase has been worked out by Maier and Saupe^{96,97}. The statistical model is based on an average internal field of the Weiss type. The nature of the assumptions concerning the intermolecular forces giving rise to liquid crystallinity is a very important feature of this theory. Maier and Saupe give convincing evidence that the forces predominantly responsible for parallel orientation in the nematic phase are the dipole-dipole dispersion forces which are highly angularly dependent because of the anisotropy of the optical transition moments of the elongated aromatic molecules. They introduce a parameter S , a typical order-disorder type scalar quantity, which varies from 0 (isotropic liquid) to 1 (perfectly ordered nematic phase). The theory yields a first order phase transition and predicts that the minimum value of S at the transition will be 0.32. Also, a reduced equation of state is obtained which is proposed to be universally valid for nematic compounds. These predictions have, at least qualitatively, been borne out by ordering experiments on a few compounds by NMR techniques. Saupe has also used the thermodynamic theory to obtain expressions for the temperature dependence of the elastic constants by relating them to the order parameter⁹⁸. The statistical theory of Maier and Saupe is the first serious attempt to study the liquid crystal phase in terms of molecular theory. The advantages and limitations of the internal field model, which amounts to the assumption of interactions of infinitely long range, are well known in statistical mechanics. We would expect that certain thermodynamic properties, such as heat capacity, would not be well determined by a model based on the internal field. This is borne out by the experimental measurements of Arnold⁹⁹. Cotter and Martire¹⁰⁰ have recently attempted to take account of short range interactions by treating the nematic isotropic transition of a system of rigid rods in terms of

a lattice model. Intermolecular attractions were accounted for in terms of a segmental interaction energy parameter. The model is able to explain the concurrent decreases in transition temperatures and increases in enthalpy which occur in ascending homologous series of nematic compounds.

It is apparent that the statistical treatment of phase transitions and order in liquid crystals based on molecular models is only in the beginning stage. It is surprising that statistical mechanics has only recently been applied seriously to these systems.

2. Thermodynamic Measurements

Most of the experimental thermodynamic studies have centered about nematic or cholesteric compounds in homologous series. Recent measurements have been reviewed by Porter, Barrall and Johnson^{101,102}. Calorimetric measurements using the method of differential thermal analysis and differential scanning calorimetry have been reported by Barrall, Porter and Johnson¹⁰³⁻¹⁰⁶ and by Ennulat^{107,108}. The most significant thermodynamic studies have been carried out in an important series of papers by Arnold et. al.¹⁰⁹⁻¹¹⁶. Arnold uses the method of adiabatic calorimetry for the determination of heat capacity and latent heats. We can summarize the results of the thermodynamic studies in a few general statements. The entropy changes of nematic-isotropic and cholesteric-isotropic transitions are approximately the same. This is in agreement with the accepted interpretation regarding the similarity of these phases. In homologous series, aside from small odd-even alternations, there is a general tendency for the transition entropy to increase with increasing molecular weight. A general correlation is observed¹⁰² in which the mesophase-isotropic entropy is roughly 2 percent of the total for all entropies from solid to isotropic liquid. Smectic-isotropic transitions are usually much larger, roughly by a factor of ten. For intermediate transitions, the entropy change for transition from smectic B to smectic C is usually greater than that for smectic C to smectic A.

One of the serious problems in this area is the lack of data on compressibility and thermal expansion coefficients. P-azoxyanisole⁹⁷ is the only compound for which these data are available

The heat capacity curve for the nematic-isotropic transition strongly suggests contributions from pretransition effects. It seems to be established that mesophase transitions are more extended than, for example, the melting transition. Torgalkar and Porter have discussed pretransition effects in liquid crystals according to the Frenkel heterophase fluctuation theory. Anomalies in physical properties near mesophase transitions have been observed in measurements of NMR relaxation times¹¹⁷, coefficients of expansion¹¹⁸, ultrasonic absorptions^{119,120}, viscosity¹¹⁸, gas chromatographic retention times¹⁰⁴, surface tension¹²¹ and magnetic flow birefringence¹²². Pretransition effects on the electro-optical properties of nematic liquid crystals have been studied recently by Tsvetkov and Ryumtsev¹²³. Heterophase fluctuations are expected to be most pronounced under conditions where latent heats are very small and there is considerable similarity between the two phases. Mesophase transitions are exactly of this type and provide a fertile field for the study of fluctuation phenomena.

D. IMPORTANT PHYSICAL PHENOMENA IN LIQUID CRYSTALS

1. Viscosity and Diffusion

The literature on both of these two topics is meager although in the case of viscosity some significant work has been done both experimentally¹²⁴⁻¹²⁷ and theoretically³³⁻³⁶ which illustrates the unusual characteristics of this quantity in liquid crystals. In the case of capillary flow or flow of thin films the motion of the liquid crystal is markedly dependent on the preparation of the surface of capillary walls or glass slides¹²⁸. The detailed methods which have been used in preparing surfaces are more or less "black magic". Vigorously rubbing a surface in one direction has the effect of aligning the preferred direction of molecular orientation parallel to the direction of the rubbing at the surface. In the case of p-azoxyanisole perpendicular orientation at the surface has been obtained by washing the glass in a sulfuric acid - dichromate cleaning solution and rinsing in distilled water.

Measurements of the viscosity, η , in p-azoxyanisole using simple capillary flow techniques show the value of η to vary by roughly a factor of five in small capillaries in which the surfaces have been prepared in the two different methods described above¹²⁸. Increasing the diameter of the capillary as well as increasing the flow rate decreases the disparity in the measurement. Measurements of the viscosity of p-azoxyanisole in the nematic phase oriented in a magnetic field show that the field strength also has an effect on the measured viscosity¹²⁶.

Aside from the anisotropy and surface orienting effects, the flow of nematic liquids appears not to be much different than that of isotropic liquids¹²⁸. Their flow seems to follow Poisseuille's law and no large changes in viscosity appear at the nematic isotropic transition.

Smectic liquid crystals on the other hand are more unusual. A carefully melted sample on a proper surface will form a terraced droplet with layers that slide easily over one another. Two glass slides with a smectic liquid sandwiched between may slide over one another easily or with considerable difficulty depending upon the molecular orientation at the surface. A similar observation has been made with capillary flow where it has been observed that at high flow rates smectic liquids flow as freely as isotropic liquids¹²⁹. Aside from observations such as these, little viscosity work has been done in the smectic phase. A recent paper by Helfrich¹³⁰ has theoretically treated smectic flow in capillaries. From his work it appears that all of the flow takes place near the surface. That is, the motion of the liquid crystal should be visualized as that of a plug sliding through the capillary.

The flow of cholesteric liquid crystals is more complicated and has been studied very little^{131,132}.

To the authors' knowledge, there have been no reported measurements of the self-diffusion constant in liquid crystals although some preliminary work is being done with regard to the diffusion of solute molecules in liquid crystals. It has recently been determined, for example, through the use of the Mössbauer effect that solute molecules are rigidly bound between

the layers in a smectic liquid crystal¹³³. The Mössbauer effect, on the other hand, vanishes in the nematic phase indicating translational freedom in this phase as expected. Experiments related to the diffusion constant of solutes in nematics are currently underway at the Liquid Crystal Institute at Kent State University. These experiments involve synthesis of compounds in nematics as well as pulsed NMR studies. Results from this work are not yet in a stage to be reported in the literature, however, pulsed NMR work indicates that a "spherical" solute molecule (tetramethylsilane) diffuses in a manner which is not strongly anisotropic.

2. Molecular Ordering and Magnetic Resonance Studies

Aside from optical measurements, perhaps the most widely used technique in liquid crystal studies in recent years has been that of magnetic resonance. Since the early 1960's a vast amount of work has appeared in the literature in this area. Some of this work is quite significant in understanding molecular order in liquid crystals. On the other hand, in a large percentage of these papers the nematic phase is used only as a matrix in which to order and study a particular molecule¹³⁴⁻¹³⁷. Many of these papers, while important in molecular configuration studies, contribute little to the understanding of liquid crystals. We have made an attempt to search through the literature and sort out the work which has bearing on the liquid crystalline phase. Assuming that in general the reader will have little acquaintance with NMR, we have not included many of the details of these measurements however, only briefly review their results as they pertain to liquid crystals. Spin-lattice relaxation is not included in this section but in the section on collective phenomena and diffusion.

Both nuclear magnetic resonance, NMR, and electron paramagnetic resonance, EPR, are sensitive to the mean orientation of the liquid crystal molecule or a solute molecule dissolved in the liquid crystalline phase, whichever is being observed. The most common way of expressing this order is through the use of the order matrix originally introduced by Saupe¹³⁸. This matrix describes a rectangular coordinate system with axes x_i ($i = 1, 2, 3$)

fixed to the molecule relative to some preferred direction of orientation \mathbf{N} . The unit vector \mathbf{N} is what we shall refer to as the nematic director. If θ_i is the angle of the i^{th} axis relative to \mathbf{N} , then the matrix elements are given by

$$S_{ij} = \frac{1}{2} \langle 3 \cos \theta_i \cos \theta_j - S_{ij} \rangle$$

$$i, j = 1, 2, 3 \text{ and } S_{ij} = \begin{cases} 0 & \text{for } i \neq j \\ 1 & \text{for } i = j \end{cases}$$

where the angular brackets refer to a time average. The trace of the matrix is zero so when referred to a set of principal axes the matrix reduces to, at most, two elements. Liquid crystal molecules are typically long and the order can be adequately described by one element. If x_3 is chosen to be along the molecular axis, the approximation can be made that $S_{11} \approx S_{22} \approx S_{33}/2 = S/2$ where

$$S = \frac{1}{2} \langle 3 \cos^2 \theta_3 - 1 \rangle$$

The ordering parameter, S , then varies between 1 and 0, depending upon whether there is perfect order or no order at all. Typical values of S in nematic phase range from 0.7 to 0.3 for liquid crystal molecules as the temperature of the sample is varied from the freezing point to the isotropic liquid where the value of S abruptly goes to zero. It has been shown in EPR studies that if one dissolves very long molecules, longer than the liquid crystal molecules themselves, in the nematic phase they may approach nearly perfect order, $S \approx 1$. On the other hand, a nearly spherical solute molecule will show $S \approx 0$. As a matter of fact, a molecule that has tetrahedral symmetry which would not be thought to order at all, will show a measurable value for S . It is believed that a liquid crystal solvent distorts the molecular shape of a solute molecule and thereby orders it.

The success of NMR in studies of molecular order in liquid crystals is due to the rapid translational and orientational diffusion of the molecules in these phases¹³⁹⁻¹⁴². As a result, the NMR spectrum depends only upon the time averaged magnetic interactions between the nuclear spins within the molecule. Interactions between the spins of neighboring molecules average to zero. The width of the NMR spectrum, distance between splittings or square root of the second moment are each directly proportional to the amount of orientational averaging of \underline{S} . Knowledge of the configuration of the molecule allows a measurement of this quantity. Often the configuration of the liquid crystal molecules is not known with sufficient precision to obtain a good measure of \underline{S} . Values of \underline{S} have been determined, however, in a number of compounds with sufficient accuracy to compare with existing theories on mechanisms responsible for molecular order in liquid crystals^{143,139,140}. It has been found that Saupe's theory^{96,97} based on dispersion interactions is generally in good agreement at the low temperature end of the nematic phase. Near the isotropic transition deviations from this theory become pronounced.

In order to test the influence of other mechanisms on molecular order such as the electric dipole moment of a molecule or molecular shape, some experiments have been performed using solute molecules¹⁴⁴⁻¹⁴⁶. If the solute molecules are sufficiently simple their resolved NMR spectrum may be observed on top of the broad diffuse spectrum of the liquid crystal¹⁴⁷. Using high resolution techniques, the degree of order of the solute molecule can be measured with extreme precision. Values of \underline{S} are typically quoted out to the fourth and fifth place past the decimal. The degree of order has been measured for fluorinated benzenes and chlorobenzenes dissolved in liquid crystals. These molecules possess permanent electric dipole moments. The compounds were dissolved in nematic solvents that had either positive or negative dielectric anisotropies. If the electric dipole moment had had a strong effect on molecular order it was expected that there would have been a large variation in relative average orientation in the different solvents since the dipole moment would have tended to be in the direction

of the largest dielectric susceptibility. Little variation was reported indicating dipole-dipole forces are of minor importance in molecular ordering.

Variations in ordering among different fluorobenzenes and chlorobenzenes in the same solute could be attributed to dispersion type interactions as well as molecular shape.

A question that often arises with regard to nematic liquid crystals is what is the angular distribution of the long axis of the molecules about the nematic director \mathbf{N} . Values of \mathbf{S} suggest that at any instant of time there will be a rather large distribution in angle, some 20-40 degrees about \mathbf{N} . If dispersion forces are dominant it is predicted that the following distribution function⁹⁶ will give the probability of finding a molecule with its major axis making an angle θ from the nematic director:

$$F(\theta) \propto e^{\alpha \cos^2 \theta}$$

where α is a constant of the material and also depends inversely on temperature. The form of this function has been confirmed somewhat indirectly in dielectric relaxation¹⁴⁸ measurements. Recently, however, through the use of Electron Paramagnetic Resonance, EPR, techniques the distribution function has been measured directly¹⁴⁹⁻¹⁵⁰. In order to describe the EPR measurement it is necessary to briefly describe the conditions under which EPR spectra are observed. Since compounds which show liquid crystallinity are not, in general, paramagnetic, this technique is primarily limited to solute studies where the solute molecule contains an unpaired electron spin¹⁵¹. The concentration of the solute required for EPR is considerably less than that needed for NMR work. Mole fractions less than $\sim 10^{-3}$ give observable spectra¹⁵²⁻¹⁵⁴. The ultimate reason for this increased sensitivity is the large value of the Bohr magneton ($\sim 10^3$ that of nuclear magneton). In nematic liquid crystals of normal viscosities the observed EPR spectrum is motionally averaged as is the case of NMR¹⁵⁵. In viscous nematics, on the other hand, the long axis of the solute molecule is not reorienting about the nematic director at a sufficient rate to motionally average the EPR spectrum¹⁵⁵. This may be viewed in terms of a correlation time τ_c which is roughly a

measure of time over which there persists some correlation within an assembly of molecules. Depending upon the magnitude of τ_c the average recorded by EPR will be either a special or time average depending upon whether $\tau_c < 10^{-9}$ sec or $\tau_c > > 10^{-9}$ sec. In nematic liquid crystals with large temperature ranges in the nematic phase such as bis (4'-n-octyloxybenzal)-2-chloro-1, 4-phenylenediamine the EPR spectra for a paramagnetic solute will be motionally averaged at the high temperature range near the isotropic transition¹⁵⁵. On the low temperature end of the nematic range the EPR spectra will have the appearance of that seen in a glassy solid indicating no averaging effects¹⁵⁵.

The distribution function $f(\theta)$ has been measured for the paramagnetic solute vanadyl acetylacetone (VAAC) dissolved in n-propyl 4'-methoxybenzylidene-4-amino- α -methylcinnamate which shows the glassy or spacially averaged EPR spectrum at room temperature¹⁴⁹. This compound will orient in an applied electric field with the long molecular axis in the direction of the field¹⁵⁰. For EPR measurements it is necessary to have the nematic sample in a magnetic field which will also tend to orient it in a direction determined by the direction of the magnetic field. However, in an electric field of 2 kV/cm the nematic molecule will retain its orientation along the direction of the electric field when placed in the competing magnetic field. From theoretical arguments it has been shown that the intensity of one of the lines in the EPR spectra is proportional to $f(\theta)$. By rotating the direction of the electric field and hence the liquid crystal within the magnetic field the distribution function was determined as a function of θ directly by measuring the intensity of the EPR line. The fit between the measured distribution and $e^{\alpha \cos^2 \theta}$ was found to be remarkably good.

In the section entitled Collective Phenomena it will be shown that frequencies typical of NMR frequencies correspond to the frequencies of the collective order fluctuations near their high frequency end, that is at wavelengths $\lambda \sim 10$ molecular lengths. This is at the short wavelength cutoff. EPR frequencies are several orders of magnitude higher corresponding to wavelengths considerably less than the cutoff for the collective modes so that one would not expect to observe collective phenomena in EPR relaxation studies. Paramagnetic relaxation of VAAC in p-azoxyanisole has shown this

to be the case¹⁵⁶⁻¹⁵⁸. These measurements, however, have been shown to be sensitive to the distribution function $f(\theta)$. From this work the function $e^{\alpha \cos^2 \theta}$ appears to adequately describe paramagnetic relaxation over a wide range of temperatures.

In solute studies using techniques other than NMR or EPR it is often not altogether clear whether a solute goes into solution as an individual molecule or solid microcrystalline particle. To the authors' knowledge there is no EPR or NMR literature which studies small particles rather than molecules in solution. It has been speculated in some Mössbauer studies that particles instead of individual molecules have been observed. However, the Mössbauer effect has never been observed in the nematic phase¹⁵⁹. If small particles containing more than 10^5 molecules were suspended in a nematic solution the Mössbauer effect would be observed.

Solutes in sufficient quantity will drastically alter (usually lower) the temperature of the nematic--isotropic transition^{133,152,160-163}. They may also broaden the temperature range over which the transition occurs¹³². At large concentrations the liquid crystal phase may be destroyed altogether. It has been shown²²¹, however, that the degree of order as a function of reduced temperature, $T/T_k(100)$, where T_k is the temperature of the clearing point on the absolute scale, is independent of the concentration of the solute. This is true provided the phase is not destroyed.

It perhaps should also be mentioned that EPR or NMR spectra cannot be used to determine the existence of swarms. The spin Hamiltonians¹⁶⁴ give the same result for the spectra whether the continuous or swarm model is used.

There are many cases in basic research where a liquid crystal; nematic, smectic or cholesteric is used as an ordering matrix to study phenomena not directly related to the liquid crystal phase. An example is the ordering of molecules in order to study their structure using NMR. As mentioned earlier, the literature is meager on cases where liquid crystals are used to order solid particles; however, there are research groups (Orsay Liquid Crystal Group, Orsay, France) who are working on this kind of project. At

any rate the liquid crystal has enormous potential in basic or applied work in this respect for ordering particles or isolated molecules. When used as an ordering matrix it is often preferred to have the liquid crystal uniformly ordered. That is, the director N be uniform throughout the sample such as to have a "monocrystal". In nematic liquid crystals this can be attained quite readily by use of a moderate magnetic or high frequency ac electric fields^{66,67,69}. The use of dc electric fields often causes turbulence problems and does not bring about uniform alignment^{140,166}. Viscous nematics¹⁶⁷, once aligned in a magnetic field will often retain their alignment after being extracted from the fields. Nematic liquid crystals, however, eventually lose in about 24 hours their uniform alignment. Smectic liquid crystals, on the other hand, are much better in this respect^{159,168}. Some smectic compounds, once aligned in a field have been known to remain perfectly aligned several days out of the field. A difficulty often arises, however, in the case of smectics in that it is not always possible to induce uniform alignment or form a "monocrystal".

Compounds which exhibit a nematic in addition to the smectic phase are usually good candidates for forming monocrystals¹⁵⁹. In these compounds the liquid crystal can be aligned in the nematic phase then while aligned the temperature of the sample lowered into the smectic phase at which case the alignment becomes "locked in". In order to form a "monocrystal" directly from the smectic phase, magnetic fields greater than 20,000 G are usually needed¹⁶⁸.

3. Light Scattering From Cholesteric Systems

As described in another section, the nematic phase strongly scatters light as a result of long range order fluctuations. Cholesteric liquid crystals which are really a special case of the nematic phase show additional scattering phenomena. The optically active molecules of these cholesteryl derivatives orient with their long axes on the average parallel to one another in the same manner as a nematic. But unlike the usual nematic phase there exists a slight twist about an axis perpendicular to the preferred direction of

orientation or local symmetry axis. The twist is gradual and produces a long wavelength periodic helical structure. As a result of this helical structure these systems show some unusual optical phenomena^{81,162-165}. When exposed to white light the cholesteric structure scatters the light to give an iridescent color with a wavelength which varies with the temperature and angle of incidence of the incoming light. The angular dependence of the diffracted wavelength has been shown to approximately follow Bragg's law. The diffracted light is also circularly polarized and produces a high optically rotary effect. The wavelength of the scattered light changes with temperature⁸³ in a way that depends on the composition of the sample. There are some cholesteric systems in which the color of the scattered light will transcend the entire visible spectrum in a fraction of a degree centigrade.

Some cholesteric liquid crystals have a right hand twist to their helical structure while others show a left hand twist. If mixed in the proper proportion the mixture will have no macroscopic twist at all at a particular temperature.

This structure is evidenced by a change in sign of optical rotary effects as this temperature of the mixture is crossed. This effect has also been observed with NMR techniques^{87,173,174}. If the anisotropy in the magnetic susceptibility is such that the pitch axis is aligned parallel to the magnetic field, it is possible to observe the resolved NMR spectrum of a solute molecule dissolved in a cholesteric liquid crystal. The spectrum becomes sharper and better resolved if a compensated mixture of opposing helicities is used with the solvent. It is interesting, however, that the spectrum observed in a compensated mixture where no macroscopic helicity is present is not the same as the spectrum observed for the same solute molecule dissolved in a normal nematic liquid crystal. It has been speculated that although no macroscopic helicity may be present the solute molecule may still experience a local helical environment.

Dissolving a cholesteric compound into a nematic liquid crystal will convert the normal nematic structure to that of a cholesteric structure.

The resulting cholesteric structure can be reconverted back into the nematic structure by the application of a magnetic⁸⁶ or electric field. If the anisotropy of the magnetic susceptibility is such that the pitch axis is perpendicular to the direction of the magnetic field and the magnetic field is sufficiently strong the helix will unwind giving back the normal nematic structure. These effects have also been observed with NMR. Normally it is impossible to observe the resolved spectrum of a solute molecule dissolved in a twisted structure with the pitch axis perpendicular to the magnetic field. Making the pitch infinite by increasing the magnetic field strength makes the spectrum visible⁸⁶.

4. Collective Phenomena

An area in liquid crystals which has caught the attention of several workers in recent years has been that of collective order fluctuations¹⁷⁵. These collective modes are responsible for the strong scattering and depolarization of light^{176-179,22} as well as the relatively short nuclear spin-lattice relaxation times^{179,180} observed in nematic liquid crystals. The milky or turbid appearance of the nematic phase is a direct result of these collective modes in that their wavelengths extend over several hundred molecular lengths comparable to that of the wavelength of light.

A common error often seen in the literature is that authors tend to attach these fluctuations directly to the long axes of the molecules. However, one should visualize these fluctuations not in terms of the molecules themselves but in terms of a director which we shall refer to as the nematic director. Physically the nematic director is the preferred or average direction of the major axis of the rod-like molecules. The molecules themselves or perhaps small groups of the molecules reorient in a hindered fashion about the nematic director, \underline{N} . The long axis of the molecules will swing through rather large angles $\sim 40^\circ$ about the nematic director. The correlation times for these reorientations are short $\sim 10^{-10}$ sec as if evident from electron paramagnetic spin resonance studies¹⁵⁵. It is not these molecular reorientations that are of interest here, but rather small fluctuations in the nematic director.

Properties of these fluctuations can be described by some quite simple relationships. The thermal amplitude of a mode of wavevector q is given by kT/Kq^2 where k is the Boltzmann constant and K is the Frank deformation²³ or elastic constant for a nematic liquid, and T is the absolute temperature. The frequency spectrum can be written approximately as

$$\omega(q) \sim i Kq^2/\eta \quad (1)$$

where ω is the angular frequency and η is the viscosity. As the frequency is pure imaginary, the modes are non-propagating. That is, when the nematic director is thermally disturbed it returns to its equilibrium direction without any oscillations and with a time constant

$$\tau_q \sim \eta/Kq^2. \quad (2)$$

Nuclear spin-lattice relaxation experiments (to be published by J. M. Doane) indicate a short wavelength limit near 10 molecular lengths for these collective modes in the nematic phase. This is analogous to the Debye dispersion relation in solids which fails for wavelengths of the order of the lattice parameter. The lattice parameter in a liquid crystal, however, is not so well defined.

The nuclear spin-lattice relaxation time, T_1 , is a measure of the rate at which energy is exchanged between the nuclear spins and the lattice. The magnitude of T_1 depends on the Fourier components of the order fluctuations at the nuclear Larmor precession frequency, $\sim 10^8$ rad/sec. More specifically, T_1 is calculated¹⁸¹ by taking the Fourier transform of the correlation functions as described by the relaxation spectra given above. It turns out that normal T_1 measurements are made in the region which is close to the cutoff wavelength, λ_c , for the fluctuation modes. This can be appreciated by substituting in the numbers characteristic of p-azoxyanisole into the cutoff expression

$$i\omega_c \simeq Kq_c/\eta \quad (3)$$

obtained from the equation (1) above where $q_c = 2\pi/\lambda_c$. Taking $K \sim 10^{-6}$ dynes, $\eta \sim 10^{-1}$ poise and $\lambda_c \sim 200 \text{ \AA}$ or 10 molecular lengths yields an $\omega_c \sim 10^8$ rad/sec which corresponds to the Larmor precession frequency. Either low frequency T_1 measurements or light scattering measurements $\sim 5000 \text{ \AA}$ are therefore necessary to study the fluctuations as described by the expression above.

In the presence of magnetic field the relaxation spectrum in equation (2) above must be modified to^{175,182}

$$\tau_q \sim \eta / (Kq^2 + \chi H^2) \quad (4)$$

where χ is the anisotropic part of the molecular diamagnetic susceptibility and H is the magnetic field. Since typical values of χ are $\sim 10^{-5}$, large magnetic fields $\sim 10^4$ to 10^8 G are required in order to make the effect observable in light scattering or spin-relaxation experiments.

Not included in the simplified eigenfrequency expressions we have written down above are six hydrodynamic constants introduced in a theoretical treatment by Leslie³⁵. These constants appear explicitly in the more exact expression for the frequencies, however their values have not yet been reported in the literature. Light scattering experiments by the Orsay Liquid Crystal group are currently underway which should give values for these parameters as well as values for the Frank deformation constants¹⁶.

Mentioned very little in the literature is the fact that the relaxation time of these fluctuation modes could be strongly limited by diffusion in some compounds¹⁸¹. An estimation of the importance of translational diffusive motion be made if one assumes this motion to be uncoupled to the orientational modes. If the molecules adiabatically diffuse through the nematic liquid then the relaxation spectrum becomes

$$\tau_q \sim \eta / (Kq^2 + Dq^2/\eta) \quad (5)$$

Although the diffusion constant, D , has not been measured in nematic liquid crystals, its value is estimated to be $D \sim K/\eta$ in compounds such as p-azoxyanisole.

This means that diffusion could strongly limit the lifetime of the orientational modes.

It has been argued and recently confirmed experimentally that collective modes exist in the isotropic phase¹⁷⁴ in the vicinity of the nematic-isotropic transition. This can be understood by the small latent heat at the nematic-isotropic transition which in turn suggests that a large amount of short range or local order should remain above the transition. These short range fluctuations have been described by de Gennes¹⁸³ in terms of a coherence length, ξ , in which case the thermal amplitude for these modes becomes $\sim kT/K(q^2 + \xi^{-2})$ and the relaxation spectrum becomes $\tau_q \propto \xi^2$. The Landau mean field theory predicts $\xi \propto (T - T_k)^{-\frac{1}{2}}$ where T_k is the nematic-isotropic transition temperature. This theoretical treatment has been recently confirmed by a spin-lattice relaxation experiment (to be published by P. Cabanne and G. Clark) in the isotropic phase.

E. CHEMISTRY

All aspects of the study and known applications of liquid crystalline behavior have been reviewed with increasing frequency in the decade and a half since the review articles of Chatelain¹⁸⁴ and of Brown and Shaw³ thoroughly covered the field^{10,135,140,185-195}. The monograph by Gray⁴⁰ and the two volumes of Proceedings resulting from the First and Second International Conferences on Liquid Crystals^{196,197} held at Kent State University in 1966 and 1968 provide good overall coverage of the state of research up to 1969.

Little advance over the concepts presented by Gray⁸ has been made with respect to correlation of mesomorphic behavior with changes in molecular structure. Most works reporting the syntheses of new systems of mesomorphic compounds still describe these relationships based on the qualitative and semi-quantitative principles discussed by Gray.

Similarly much of the synthetic work has been principally aimed at either filling in data for homologous series for which some member had previously been identified as possessing a mesophase, or in modification

of terminal groups on some previously established mesomorphic system. Most work of the latter type has centered around preparation of modified anils.

There has been a fair amount of activity concerned with the preparation of mixture systems with an aim to improve physico-chemical properties useful to applications. A number of interesting observations have come out of this work, as might have been expected, mixed systems often result in both lowering of the crystal-mesophase transition temperature and in extending the range of mesophase stability. Of great interest is the demonstration that a subclassification scheme may be derived to describe polymesomorphic substances which is based on phase diagrams constructed for mixed systems.

An area of application that has been of interest to organic chemists is the use of liquid crystalline substances as stationary phases in gas chromatographic separations.

Each of these topics is reviewed below; coverage of the literature extends through March, 1970.

1. Correlation of Molecular Structure With Liquid Crystallinity

The most systematic work in this area has been done by Gray⁴⁰. He has established criteria which may be used not only to explain observed phenomena but also for predictive synthetic planning. Beyond the detailed discussions given in his monograph and numerous papers on the subject, the two papers presented at the First and Second International Conferences on Liquid Crystals at Kent State University in 1965 and 1968, provide the best summary and review of the subject through early 1968^{198,199}. Comments included here serve to iterate his conclusions and to supplement them with work published through early 1970.

Within any given structural system of mesomorphic compounds, for example, azobenzene derivatives or cholesteryl esters, large variations in molecular structure may cause marked changes in liquid crystalline behavior. A systematic study in which small regular changes may be made is more useful. Mesomorphic compounds fit a generalized structure in which there is a longer

relatively rigid axis in one direction, limited breadth and thickness and with dipolar functional groups at several places along the longer axis;

Figure 1. Each of these factors play a role in defining whether a compound

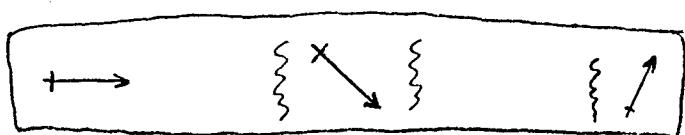


FIGURE 1. IDEALIZED MODEL OF MESOMORPHIC COMPOUND MOLECULE

is mesomorphic and whether it has a smectic or nematic mesophase or both. It is generally accepted now that the cholesteric mesophase is a special case of the nematic in which molecular (optical) asymmetry is present. (Reference 199, page 166.)

Alterations in structure are most easily considered in context with the following qualitative picture of changes which occur during phase transitions:

(1) Crystal to smectic - Molecules which are held together in a parallel regular arrangement by both lateral and terminal attractive forces in a crystal lattice undergo a loosening of terminal forces due to increased thermal motions. This allows a sliding of layer planes containing regular parallel arrangements of molecules (these may be straight or tilted normal to the sliding plane; a tilt axis may be regular or alternating in successive planes).

(2) Smectic to nematic - A loosening of primary lateral attractions between molecules must occur so that molecules may slide longitudinally over one another. There must still be sufficient attraction to prevent complete disordering.

(3) Nematic to isotropic - Thermal motion increases to the point where random orientation occurs.

Obvious modifications of these pictures can explain crystal-nematic and smectic-isotropic changes. Smectic polymorphism may occur if there are more than one stable parallel packing arrangement for molecules within a layer, Figure 2, for example.

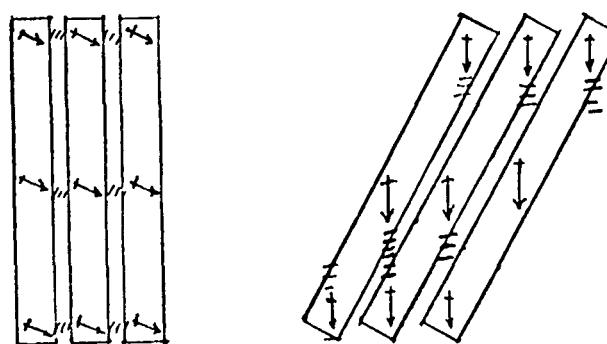


FIGURE 2. TWO POSSIBLE STABLE PARALLEL ARRANGEMENTS FOR LINEAR MOLECULES WITH MULTIPLE DIPOLES

Changes in structure that alter either lateral or terminal attractive forces between molecules would be expected to alter mesophase stability. The extent of alteration as a function of substituent changes would measure the relative importance of these attractive forces.

Lateral Substitution

This may affect thermal stability of mesophases in two opposing ways: (a) the "bulk" of a substituent will reduce attractive forces between adjacent molecules by increasing separation, (b) to the extent a substituent increases local polarity and polarizability, it will increase attractive forces between molecules.

Gray has suggested a molecule may be imagined as occupying a cylindrical sheath which accommodates its greatest breadth. If substitution does not increase this breadth it may contribute under (b) and raise the transition temperatures for phase changes; generally such an effect is only of importance for smectic mesophases. The usual effect of lateral substitution occurs under (a) and will operate to lower phase transition temperatures for both nematic and smectic mesophases.

Examples include:

(1) 3'-Substituted-4'-n-alkoxybiphenyl-4-carboxylic acids

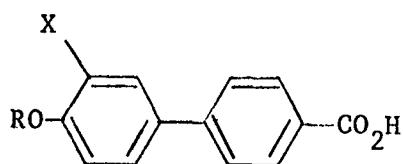


exhibit a steady decrease in nematic-isotropic transition temperatures with increase in the size of X; Figure 3 shows this for the n-octyl ethers:

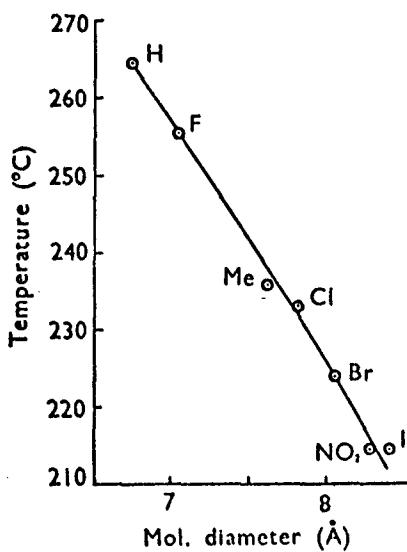
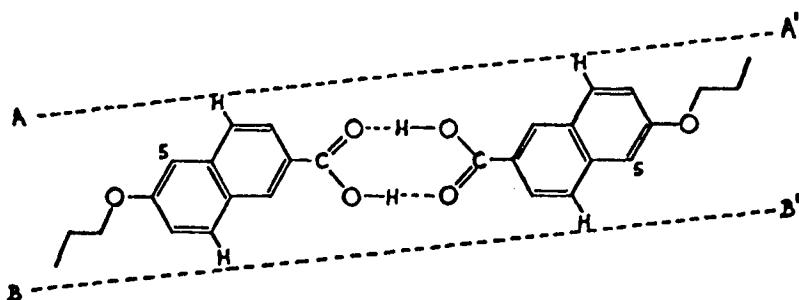


FIGURE 3. A PLOT OF MOLECULAR DIAMETER (Å) AGAINST THE NEMATIC-ISOTROPIC TRANSITION TEMPERATURES (°C) FOR 4'-n-ALKOXYBIPHENYL-4-CARBOXYLIC ACID AND ITS 3'-SUBSTITUTED DERIVATIVES. (FROM REF. 196, P. 133)

(2) 5-Substituted-6-*n*-alkoxy-2-naphthoic acids show an increase in both smectic-nematic and nematic-isotropic transition temperatures for chlorine or bromine substituents relative to the unsubstituted compound but a decrease with iodine for only the nematic-isotropic temperature of transition.



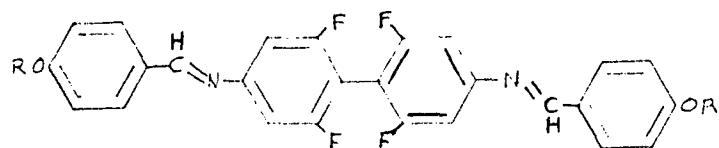
Structural representation of the dimer of a 6-*n*-alkoxy-2-naphthoic acid.

Transition Temperatures for 5-substituted 6-*n*-nonyloxy-2-naphthoic Acids

Substituent	Smectic-nematic (°C)	Nematic-isotropic (°C)
None	140	183.5
Cl	185.5	194.5
Br	180	192.5
I	157.5	182

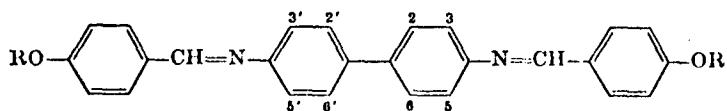
FIGURE 4. (FROM REF. 197, P. 134)

On the basis of these and other studies, Gray has shown that one may predict the average change (decrease) in transition temperatures for anils of laterally substituted benzidines, Figure 5. Lateral substitution may also function by steric inhibition of ring coplanarity; examples are those 2, 2'-disubstituted benzidine derivatives in Figure 5. Based on these findings, Gray expressed doubt⁴⁰ that the tetrafluoro derivative:



would exhibit liquid crystallinity.

Observed and Predicted Average Decreases in Liquid Crystalline Thermal Stability for some Di-, Tri-, and Tetra-substituted 4,4'-Di-(*p*-n-alkoxybenzylideneamino)biphenyls⁷



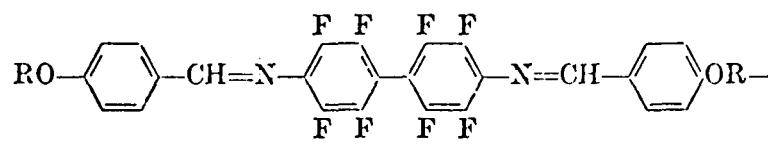
Substitution	Average decrease (C ₈ -C ₁₀) Smectic		Average decrease (C ₇ -C ₁₀) Nematic	
	Calc.	Obs.	Calc.	Obs.
3,3'-DiCl	180°	181°	96.8°	94.2°
3,3'-DiBr	223.8	203.0	116	112.4
3,3'-DiMe	220.4	—	96	90.6
2,5-DiCl	—	—	132.5	134.6
2,5-DiBr	—	—	157.2	157.7
2,5-DiMe	—	—	133.4	131.5
2,3'-DiCl	—	—	132.5	126.4
2,3'-DiMe	—	—	133.4	127.1
2,2'-DiCl ^a	—	—	132.5	160.2
2,6-DiCl ^a	—	—	132.5	152.9
2,2',6-TriCl	—	—	229	222.1
2,2',6,6'-TetraCl ^b	—	—	284	> 253.5

^a Probable extra steric effects not allowed for in calculated figures.

^b Based on n-heptyl ether only.

FIGURE 5. (FROM REF. 196, P. 136)

Goldmacher and Barton²⁰⁰ prepared the octafluoro compounds illustrated, and showed that they were liquid crystalline, however.

*Octafluoro-*

R = Me N—I 370 °C (d)

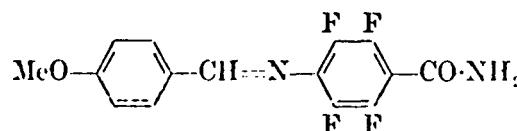
R = n-Pr S—N 210; N—I 315 °C

Unsubstituted

R = Me N—I > 390 °C

R = n-Pr N—I > 390 °C

Gray¹⁹⁹ has discussed this briefly and remarks that the appearance of a smectic phase for the n-propyl derivative is indicative of increased lateral attractions of type (b); analogous to the results for the naphthoic acids (Figure 4). This is even more striking in the case of the amides²⁰⁰:

*Tetrafluoro-**Unsubstituted*

S—I 268 °C

S—I 195 °C

Gray proposed that two of the fluorine atoms would increase breadth but that then the addition of two more fluorine atoms only increases lateral attractive forces, enhancing thermal stability.

Terminal Substituent Modifications

Replacing end groups on typical polynuclear aromatic smectic and/or nematic liquid crystalline compounds does not provide a simple correlation between trends in transition temperatures and most measures of intramolecular substituent effects (i.e. those on which linear free energy relationships are based). Rather, as should be expected, terminal substituent changes must act to modify (a) terminal intermolecular approach distances (b) intermolecular attractions due to polarizability (c) the probability that laterally attractive parts of adjacent molecules will approach one another. Two kinds

of systematic changes in terminal groups have been investigated: (1) homologation or simply increasing or decreasing the lengths of n-alkyl chains attached either directly or through other functions to an aromatic ring or steroid nucleus (2) changes in the polarity of substituents with similar group sizes. An example of the first type is illustrated by Figure 6 which presents a plot of transition temperatures vs. carbon number for the terminal groups in the series: 4-n-alkoxybenzylidene-4'-aminobenzoic acids²⁴.

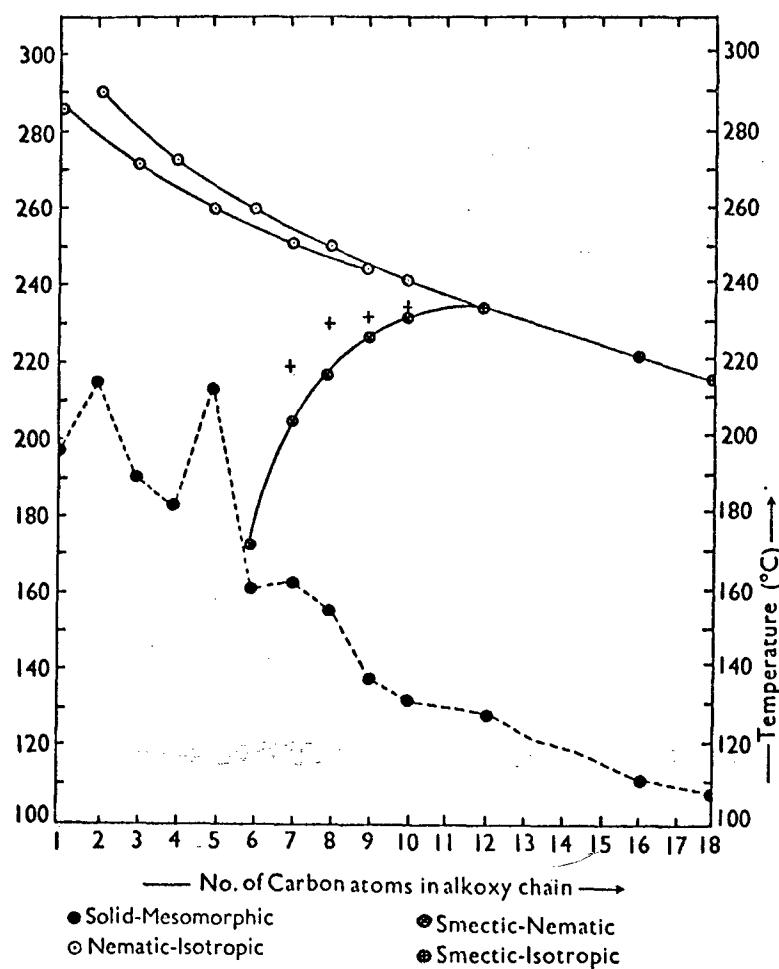


FIGURE 6. (FROM REF. 196, P. 377)

This type of plot has been described in detail by Gray¹⁸ who considers many examples and discusses the general significance. The crystal-mesomorphic temperatures for low-molecular weight members of the series show some alternation of the odd-even kind usually associated with melting points for homologues and then a smoothing out (a decline with increased molecular weight). The lower molecular weight members of the series (C_1 - C_5) have a distinct nematic mesophase while the higher members (C_{12} - C_{18}) of the series show only a smectic mesophase. Intermediate members of the series have both a smectic and a nematic mesophase, the smectic phase always occurs over the lower temperature range for which the mesophase is stable. This is consistent with an ordering more nearly analogous to that of the crystalline solid. It has usually been assumed that the mesophase-isotropic transition temperature represents the best thermodynamic parameter for correlations of any structure changes with mesophase stability regardless of the mesophase type (smectic or nematic). This may be justified since the nematic-isotropic plot and the smectic-nematic plot constitute two smooth lines which approach and become identical for higher molecular weight members of a plot such as that of Figure 6.

The data for effects of homologation on mesophase properties has been increased by the efforts of Dave and coworkers^{201,202}, Sachmann and coworkers^{203,204}, Dewar and Schroeder²⁰⁵, Arora, et. al.^{47,48,206}, Fishel and coworkers^{207,208}, Elser²⁰⁹, and Ennulat¹⁰².

2. Syntheses of Pure Mesomorphic Compounds

Kast²¹⁰ has compiled transition temperature data on thermotropic liquid crystalline systems known by early 1959. He has classified them into fourteen groups roughly based on organic functional group types used for the central part of the molecule. These are:

- I. Organic salts (fatty acid and pyridinium salts).
- II. Derivatives of aliphatic carboxylic acids (dimers).
- III. Aromatic carboxylic acids and derivatives (other than azomethine, azo- and azoxy- compounds).

- IV. Derivatives of ethers and ketones (other than azomethine, azo and azoxy compounds).
- V. Multi-nuclear hydrocarbons and derivatives (other than azomethine, azo and azoxy compounds).
- VI. Azomethine compounds (with only an azomethine group).
- VII. Azines and glyoxal compounds.
- VIII. Bis (azomethine) compounds.
- IX. Azo compounds.
- X. Azomethine, azo-compounds.
- XI. Azoxy compounds.
- XII. Azomethine, azoxy compounds.
- XIII. Disulfides.
- XIV. Derivatives of steroids.

The compounds listed in Kast's tables are merely identified as smectic, nematic or cholesteric or some combination of these. There are some discrepancies with respect to use of a homogeneous systematic nomenclature and a considerable number of the compounds listed are only published as theses or dissertations with only limited or no circulation. These latter were principally written and submitted to the Universities at Halle or at Leipzig and so cannot easily be checked to evaluate techniques used for transition temperature determinations.

A considerable amount of work could be done toward the classification of the compounds listed in Kast by the more elaborate but useful schemes worked out by Sachmann and Demus, et. al.²¹¹. These latter are based on optical textures, the comparison of melting behavior via binary-mixture phase diagram studies, or by X-ray-scattering investigations. This work is reviewed below.

Gray's monograph⁴⁰ includes some synthetic work reported in early 1961; it is more a rather complete critical survey of the known facts concerning

mesomorphic behavior up to that time but is not encyclopaedic in scope. The emphasis is on correlation of organic molecular structure with mesomorphic behavior. This includes such topics as functional group composition, homologation, molecular geometry and intermolecular attractions resulting from both permanent and induced dipoles as well as polarizability effects.

Schiff's Base Derivatives (Anils)

Various members of the anil series: 4-alkyloxybenzylidene-4'-alkylanilines have been prepared by different research groups. Chistyakov, et. al.²¹² essentially confirmed work done by Gabler²¹³ and listed in Kast's compilation (system 386) for 4-nonyloxybenzylidene-4'-toluidine; he also observed homeotropic phenomena. Kelker and Scheurle²¹⁴ prepared several of these homologues (Table 1) including 4-methoxybenzylidene-4'-n-butylaniline which is a stable room temperature nematic liquid crystal now being extensively investigated in many laboratories to take advantage of these desirable characteristics.

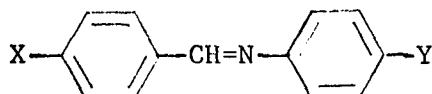
Fishel, Patel and Flandera²⁰⁷ have prepared all homologues from C₁ to C₁₈ in the two series: 4-alkyloxybenzylidene-4'-ethylaniline and 4-alkyloxybenzylidene-4'-n-butylaniline. The derivatives from C₃ to C₈ in the former series demonstrate a smectic mesophase which appears to have an ordering similar to that observed in fibrous systems (preliminary X-ray examination). Only 4-methoxybenzylidene-4'-n-butylaniline demonstrated stable mesomorphic behavior at room temperature although several members of the series could easily be supercooled to room temperatures as mesophases.

Dave and Patel²⁰¹ prepared most of the homologues from C₁ to C₁₈ in the series: 4-n-alkyloxybenzylidene-4'-n-propoxyaniline, 4-n-alkyloxybenzylidene-4'-n-butoxyaniline and 4-n-alkyloxybenzylidene-4'-n-amyloxyaniline. No unusual behavior was observed although a substantial number of these compounds were found to be monotropic. These workers²⁰² have also reported the preparation of the series 4-n-alkyloxybenzylidene-4'-aminobenzoic acids and their methyl esters. The C₁ to C₁₀ free acids exhibit nematic behavior;

smectic behavior was exhibited by the C_6 to C_{18} free acids and for the C_4 to C_{18} methyl esters. The transition temperatures were predictably high (in the range from ≈ 200 to ≈ 260 for the nematic mesophases).

Paleos et. al.²¹⁵ reported the preparation of the C_1 , C_4 , and C_{18} homologous 4-n-alkyloxybenzylidene-4'-aminostyrenes. These could not be characterized as crystalline materials and are of doubtful purity. They report transition temperatures and polymerization behavior for these compounds.

Castellano, et. al.²¹⁶ have reported the preparation of twenty-one derivatives which fit the structure I. X and Y terminal groups included

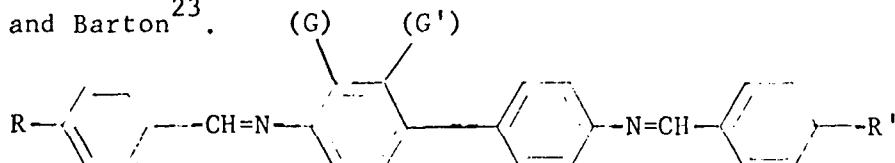


I

alkyloxy, acetamido, acetyl, acetoxy, cyano, nitro, chloro, methylmercapto and alkylacrylyl functions. Nine compounds exhibited a nematic range, six showed smectic behavior. Although these compounds were prepared in hopes of obtaining materials with a stable nematic mesophase below 100° only 4-methoxybenzylidene-4'-acetoxyaniline had reasonable characteristics (nematic over the range 83° - 110°); this compound had previously been reported by Hansen in 1907 (Kast, system 403). Mesomorphic trends for the series 4-n-alkyloxybenzylidene-4'-aminoacetophenones were discussed.

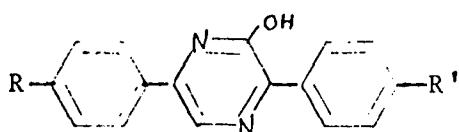
A more complete study of the two series: 4-n-alkyloxybenzylidene-4'-aminoacetophenone and 4-n-alkyloxybenzylidene-4'-aminopropiophenone are reported by Arora et. al.⁴⁸ who prepared the C_1 to C_{18} homologues. This research group has also reported the preparation of several series of di(4'-n-alkoxybenzylidene)-1,4-phenylenediamines both without and with lateral substitution (chlorine or methyl on the central 1,4-phenylenediamine nucleus). They report this series provided an extreme case of polymorphism and give evidence derived from DTA and optical measurements that the C_6 to C_{10} derivatives possess five smectic as well as one nematic mesophases^{47,206}.

Anils prepared from benzidines have been of interest since lateral substitution on the central biphenyl moiety would provide easy access to a system which could be used to investigate the effects of either or both molecular broadening or steric inhibition of ring coplanarity (Structure II). Such studies have been reported both by Gray and coworkers^{40,217,218} and by Goldmacher and Barton²³. (G) (G')

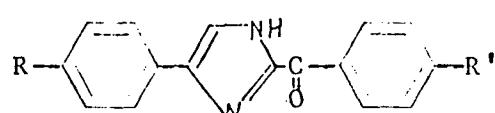


11

Schubert and coworkers²¹⁹ obtained two homologous series of mesomorphic 2,5-diphenyl-3-hydroxypyrazine derivatives, III, as by-products during the formation of imidazolylketones, IV. The latter are not liquid crystalline.



111



IV

R = R' = n-alkyl or n-alkyloxy (C₁ to C₁₀)

Most of the 3-hydroxypyrazine derivatives exhibit one or two typical smectic mesophases and the C_1 , C_2 and C_3 n -alkyloxy derivatives also possess a nematic mesophase (Figures 7 and 8).

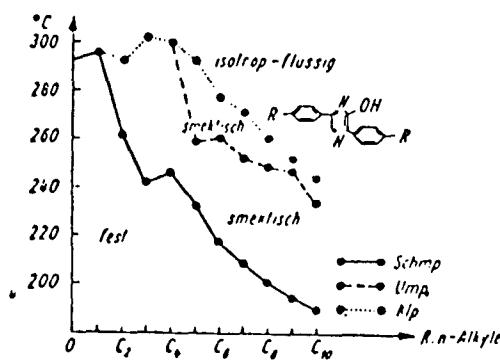


FIGURE 7. PHASE TRANSITION POINTS FOR 3-HYDROXY-2,5-BIS-(*P*-N-ALKYLPHENYL)-PYRAZINE

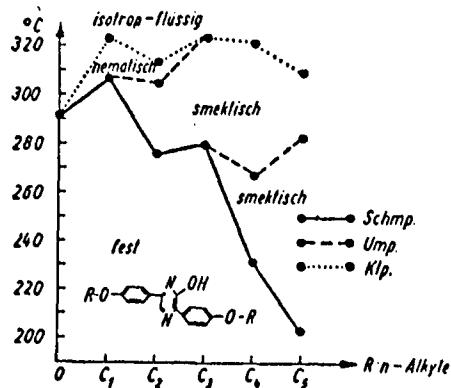
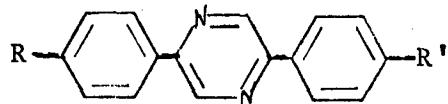


FIGURE 8. PHASE TRANSITION POINTS FOR 3-HYDROXY-2,5-BIS-(P-N-ALKOXYPHENYL)-PYRAZINE

The series of pyrazine derivatives, V, were also prepared by



$R=R'=\underline{n}$ -alkyl or \underline{n} -alkyloxy (C_1 or C_{10})

V

Schubert's group²²⁰. Both the 4- \underline{n} -alkyl and 4- \underline{n} -alkyloxy series have nematic behavior for the C_1 to $\approx C_6$ derivatives and several smectic states for the higher members of the series; See Figures 9 and 10.

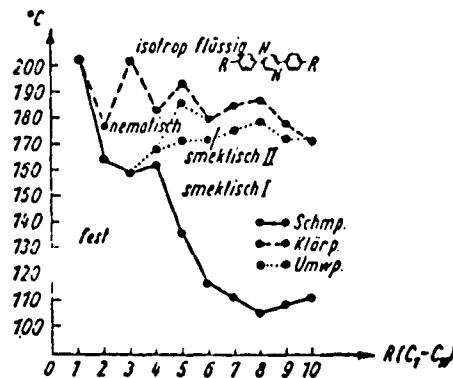


FIGURE 9. PHASE TRANSITION POINTS FOR 2,5-BIS-(P-N-ALKYL)-PYRAZINE

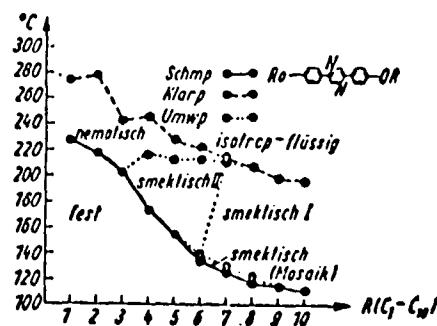


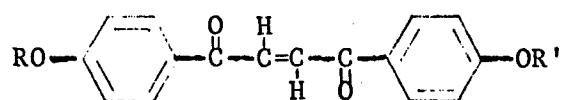
FIGURE 10. PHASE TRANSITION POINTS FOR 2,5-BIS-(P-N-ALKOXYPHENYL)-PYRAZINE

The trans-4,4'-di'n-alkyloxybenzoylethylenes, VI, with R from C_9 to C_{18} were found²²¹ to possess a smectic mésophase over a narrow temperature range in the vicinity of 100° , Table I.

TABLE I

R	Melting Point (°C)	Clearing Point (°C)
a Ethoxy	160	---
b n-Propoxy	122	---
c n-Butyloxy	118	---
d n-Pentyloxy	99.5	---
e n-Hexyloxy	97	---
f n-Heptyloxy	97	---
g n-Octyloxy	98	---
h n-Nonyloxy	98	94-87*
i n-Decyloxy	91	99
j n-Undecyloxy	93	103
k n-Dodecyloxy	93	104
l n-Tetradecyloxy	94	105
m n-Hexadecyloxy	94	106
n n-Octadecyloxy	103	103-99*
o Phenoxy	170	---

*monotropic



Markau and Maier²²² prepared the series of alka-2,4-dienoic acids and measured their transition temperatures. These are given in Table II.

TABLE II

STRUCTURE AND LIQUID CRYSTALLINE PROPERTIES

Substanz	Formel	Schmp. °C	Klärpunkt der nematischen Phase °C
Heptadien-(2,4)-säure-(1)	C ₂ H ₅ ·CH:CH·CH:CH·CO ₂ H	44	46
Oktadien-(2,4)-säure-(1)	C ₃ H ₇ ·CH:CH·CH:CH·CO ₂ H	84	nicht krist.-flüss.
Nonadien-(2,4)-säure-(1)	C ₄ H ₉ ·CH:CH·CH:CH:CO ₂ H	23 (23)	53.5 (49)
Decadien-(2,4)-säure-(1)	C ₅ H ₁₁ ·CH:CH·CH:CH:CO ₂ H	49	70
Undecadien-(2,4)-säure-(1)	C ₆ H ₁₃ ·CH:CH·CH:CH:CO ₂ H	32 (32)	62.5 (59)
Nonaen-(2)-in-(4)-säure-(1)	C ₄ H ₉ ·C:C·CH:CH·CO ₂ H	48 (46)	nicht krist.-flüss.
Nonadien-(2,4)-al-azin	C ₄ H ₉ ·CH:CH·CH:CH:CH:N· N:CH·CH:CH:CH:CH·C ₆ H ₅	103	112
Decadien-(2,4)-al-azin	C ₅ H ₁₁ ·CH:CH·CH:CH:CH:N· N:CH·CH:CH:CH:CH·C ₆ H ₅	106	121
Undecadien-(2,4)-al-azin	C ₆ H ₁₃ ·CH:CH·CH:CH:CH:N· N:CH·CH:CH:CH:CH·C ₆ H ₅	98	112

Hepta-2,4-dienoic acid is perhaps the simplest structure possessing mesomorphic behavior although the range is very small. The 9 and 11 carbon homologues had previously been prepared by Weygand et. al.²²³; the low temperature range over which these compounds exhibit nematic behavior is desirable for potential applications but unfortunately these compounds show the usual high reactivity expected of poly-olefines including polymerization, cycloaddition, etc.

Polymorphism has been investigated systematically by Sachmann, Demus and coworkers (see below). During these investigations they have synthesized a number of mesomorphic compounds which exhibit various smectic and nematic mesoforms. These include the C₁₆ and C₁₈ 4'-n-alkoxy-3'-nitrobiphenyl-4-carboxylic acids²²⁴ which were shown to possess a new smectic modification (smectic D in the Sachmann-Demus classification scheme).

Smirnov²²⁵ prepared a number of 4-isoalkoxybenzaldehyde derivatives; 4-isopropoxy- and 4-isoamyloxy-cinnamic acids were shown to possess nematic mesophases.

Kelker and Scheurle²²⁶ have prepared a number of symmetrically substituted naphthalene dicarboxylic acid derivatives as a part of a larger effort toward obtaining new materials as solvents for gas-liquid chromatography (see later).

A homologous series of 4,4-dialkaneterphenyl- α , Ω -dioic acids (with from five to eleven $-\text{CH}_2-$ groups on each end) and their methyl esters were prepared by Dehne et. al.²²⁷ and shown to possess mesomorphic behavior.

Cholesterol and other steroid derivatives, notably alkanoic and aromatic carboxylic esters have been known to possess mesomorphic properties for as long as liquid crystalline materials have been recognized. Research including synthetic studies on these materials continues; among the more recent work in this area are papers by Elser^{209,228}, Pohlmann^{229,230} and Knapp^{231,232}

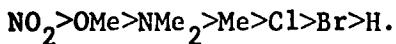
3. Mixed Systems and Polymorphism of Liquid Crystals

Gray⁴⁰ devotes a chapter in his monograph to a discussion of the liquid crystalline behavior of mixtures. A mesophase will usually occur for mixtures of two compounds which are mesomorphic in the pure state, will often occur for mixtures of a non-mesomorphic compound with one which is mesomorphic and will occasionally occur when two non-mesomorphic compounds are mixed.

In general the requirements for such mixed mesophases are similar to those for mesomorphism of a pure compound; i.e. parallel alignment of molecules which are long, flat and of limited breadth and which have specific lateral and terminal attractions which allow either two dimensional order (smectic) or uniaxial order (nematic). Usually as is true for most mixtures of organic compounds, the phase transition temperatures are depressed. Occurrence of

a mesophase depends on occurrence of a system in which the mesophase-isotropic transition temperature is not depressed below the crystal-mesophase transition. Some concern was shown in early studies toward establishing whether a homogeneous mesophase occurred for mixtures at temperatures above the transition temperature or whether there must be a temperature range over which a series of mixtures of different composition would coexist. Work by Dave and Dewar⁵⁹ appeared to support the view of a perfectly homogeneous mesophase. Arguments for and against observation of an apparently normal first-order phase transition of this sort for mixed systems are described by Gray. He comments on use of precise reversibility of mesophase-isotropic transitions and definition of boundary layers between phases as criteria of the purity of mesomorphic compounds.

Among several interesting results derived from the work by Dave and Dewar should be mentioned the observation that terminal group effects on the slopes of transition temperature versus composition plots were approximately additive. It was found possible to place substituents in an order of efficiency in giving rise to nematic behavior in a mixed system such as 4,4'-disubstituted anils dissolved in *p*-azoxyanisole. The order for terminal substituents was:



Gray reviews this work and places it in perspective with related work by his own research group and concludes that there are other factors which control the relative order for such "group efficiencies" and that the overall gross structure of the mesomorphic compound as solvent has a profound effect.

It is clear that this is a fruitful area for further research toward the objectives of both altering the temperatures for mesomorphic transitions and increasing the mesophase range and type. Further work has been done by Dave's research group²³⁴⁻²³⁸. They have added to the list of substituent group efficiencies and extended investigations into mixed systems involving a fair number of anils and some alkoxyaromatic acids.

Sachmann and his coworkers have also made extensive investigations of mixed mesomorphic systems. These have included both nematic and smectic mesophases. Demus²³⁹ reports phase diagrams for the binary systems: n-butyl 4'-ethoxyazobenzene-4-carboxylate with both (1) n-propyl 4'-methoxybenzylidene-4-amino-X-methyl-cinnamate and (2) (4'-methoxyazobenzene-4-oxy) hexanoate and (3) the mixed system of the latter two components. All three mixed systems show a nematic mesophase with an enhanced range due to formation of a eutectic composition involving depression of the crystal-nematic transition temperature.

Sachmann and Demus have attempted to derive a system for subclassification of mesophase types based on the degree of polymorphism which a given pure compound or mixed system exhibits. They have studied a large number of mixture systems and have concluded that it is possible to relate mesomorphic subclasses by texture/miscibility observations^{211,240}. Table III presents their classification scheme based on the degree and type of polymorphism exhibited by a given compound.

Their experimental methods included thermal analysis of specific compositions and the Kofler²⁴¹ contract method for identification of texture and miscibility. Phase diagrams were constructed with the aid of this information and the relationship of mesophases determined by comparison of one compound with several others. This is illustrated by the diagrams in Figure 11 i.e.: "Substance I exhibits a smectic modification, which is arbitrarily marked with the symbol S_A. Substance II exhibits two smectic phases. The binary phase diagram of the substances I and II is given in the Figure under (a). The liquid crystalline phase region of substance I exhibits an uninterrupted series of mixed liquid crystals with the high temperature phase region of substance II. By virtue of this fact alone the liquid crystalline phase of substance II is marked also with the symbol S_A. Each phase of other substances which exhibits with one of the marked phases an uninterrupted series of mixed crystals is also marked with the symbol S_A and can transfer it in the same manner to other phases.

Because of the marking of the high temperature phase of substance II with the symbol S_A, the low temperature phase must have another symbol, here arbitrarily S_B.

TABLE III

CLASSIFICATION OF POLYMESOMORPHIC COMPOUNDS ACCORDING TO SACHMANN AND DEMUS²¹¹

	c1	pt.	T ₁	T ₂	T ₃
a)	is	n			
b ₁)	is	S _A			
b ₂)	is	S _C			
c ₁)	is	n	S _A		
c ₂)	is	n		S _C	
d ₁)	is	S _A	S _B		
d ₂)	is	S _A	S _C		
e ₁)	is	n	S _A	S _B	
e ₂)	is	n	S _A .,	S _C	
f)	is	S _I	S _{II}	S _{III}	
g)	is	n	S _A	S _C	S _B

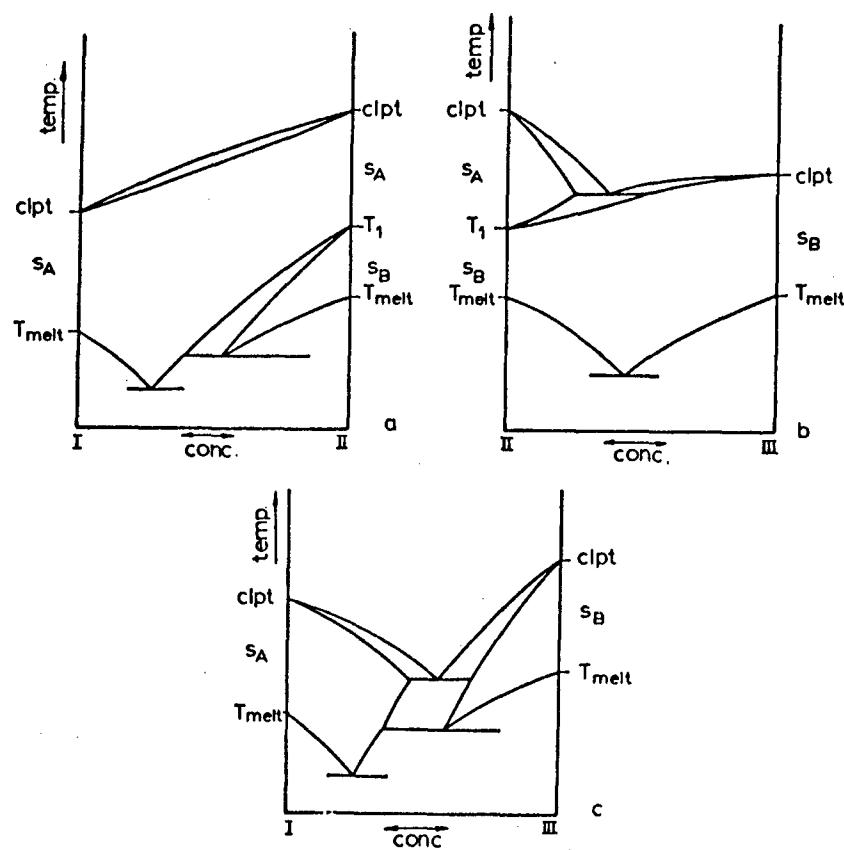


FIGURE 11

DEMONSTRATION OF THE METHOD OF MARKING LIQUID CRYSTALLINE PHASES

The relations of miscibility of substance II with substance III are given in diagram (b). The liquid crystalline low temperature phase of substance II exhibits a complete series of mixed crystals with the liquid crystalline phase of substance III and for that reason the latter phase gets the same symbol.

It is necessary for the consistent use of this method that in the binary phase diagram of the substances I and III both phase regions S_A and S_B do not exhibit an uninterrupted series of mixed crystals. Therefore they must show a behavior as given for example in diagram (c) in the figure." [quotation from reference 241].

4. Liquid Crystalline Substrates for Gas Chromatography

Use of liquid-crystalline materials as solvents in gas-chromatography excited an initial flurry of investigation after the applications reported by Kelker²⁴² and by Dewar²⁴³. The major advantage which these materials appear to have over ordinary isotropic liquid phases is their ability to separate isometric mixtures for which the components differ in geometric requirements for solubility. Thus Dewar²⁴⁴ demonstrated reasonable separations of meta- and para- disubstituted benzene derivatives on various smectic mesophases. Kelker and Schivizhoffen²⁴⁵ have written a rather extensive discussion of all aspects of this topic which covers the literature prior to early 1967. In the interim to early 1970, less work has appeared than earlier. There has been added interest in the use of glc techniques to determine thermodynamic parameters of mesophases used as solvents.

Barrall, et. al.²⁴⁶ suggested the use of a sharp break in retention times be used to identify transition temperatures of mesophases; this occurs for solutes being chromatographed at mesophase-isotropic transition points, Figure 12. Chow and Martire²⁴⁷ have concluded that glc measurements can provide thermodynamic information concerning solvent characteristics of the bulk phase for mesomorphic materials as substrates.

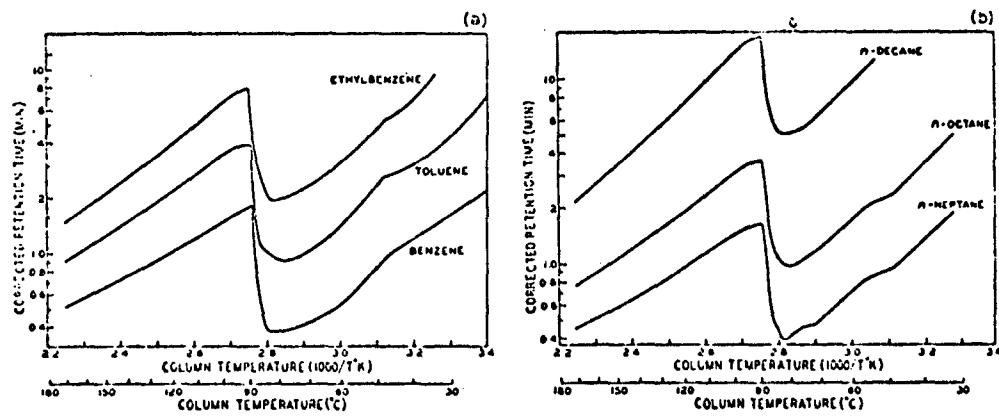


FIGURE 12

TEMPERATURE VERSUS RETENTION TIME FOR CHOLESTERYL
VALERATE COLUMN. (FROM REF. 246)

Kostev and Shopov²⁴⁸ have recently determined stability constants for complexes of olefins with 4,4'-azoxyphenetole using the latter as a glc substrate.

Kelker and Verhelst²⁴⁹ have investigated solvent solute interactions and pretransition behavior in terms of specific retention volumes for o-xylene on 4,4'-azoxyanisole, 4,4'-azoxyphenetole and their eutectic mixture composition.

Zielinski, Freeman, Martire and Chow²⁵⁰ have accomplished base-line separations of the meta and para isomers of divinylbenzene and of ethyl-vinylbenzene by glc, on 4,4'-dihexyloxybenzene. They related these results to the concept that the meta isomers have lower solubility than para isomers by thermodynamic measurements which suggested a lower enthalpic requirement for the para- isomers.

III. APPLICATIONS OF LIQUID CRYSTALS

INTRODUCTION

In 1924 one of the most prominent of the chemists in the field of liquid crystals, D. Vorlander, stated in his monograph¹ that liquid crystals could never have any practical application and could be of interest only in testing theories of the structure of matter. Since that time the situation has changed radically and many potential and actual practical applications of the unusual physical properties of liquid crystals have been discovered. Furthermore, many new uses and applications are rapidly being discovered. The recognition of the many practical possibilities has led to vastly increased activity not only in the applied science and technology of liquid crystals but also in the continuance of basic research on their properties and preparation. After lying dormant for many years the whole field has become very much alive again because of the increased recognition of the practical possibilities for liquid crystals. Many applications have reached the commercial stage. This is, specific materials for specific purposes are available commercially. The most typical example here is the use of cholesteric crystals in non-destructive testing, an application which relies on the sensitivity of the color of the liquid crystalline material to changes in temperature and stress. Some other applications are still in the development stage but require only some engineering and development to reach fruition as commercial product. An example is the use of nematic or mixed nematic and cholesteric liquid crystals in display devices. A third category is the more speculative applications; these are still in the laboratory stage and their feasibility as practical methods are yet to be proven. A typical example here is the use of liquid crystals as solvents in the synthesis of organic compounds where the reaction path depends on steric factors. Several reports on this topic have appeared in the literature but there is still no assurance that the technique will ever offer commercial advantages.

In the following sections present applications of liquid crystals will first be discussed and, where possible, their application to technology evaluated. This discussion will be followed by a section on laboratory applications, that is application of liquid crystals to the solution of problems in areas of scientific research rather than technology. Research and development needed for the eventual practical utilization of possible application will be indicated where necessary.

A. PRESENT APPLICATIONS

1. Application of the Color Sensitivity of Cholesteric Liquid Crystals

Fundamental Principles

As mentioned earlier in this report, cholesteric liquid crystals exhibit many unusual optical properties. These properties are most easily observed when the material is in the form of a thin sheet. The sheet of material behaves like an anisotropic crystal with an optical axis normal to the sheet. Linearly polarized light transmitted along the optical axis has its plane of polarization rotated through an angle that is linearly dependent upon the thickness of the material. This angle is also dependent in a much more complicated way upon the particular wavelength of the light. This optical activity is much larger in cholesteric liquid crystals than in any other known substance or class of substances. Rotation of the plane of polarization by as much as 1800° per mm has been observed for some cholesteric substances.

The most useful optical property of cholesteric materials for non-destructive testing applications is their irridescence when illuminated by ambient light. The colors observed are due to scattering within the material, the thickness of which does not affect the predominant wavelength of the reflected light. Furthermore, plane polarized light becomes circularly polarized upon scattering. The sense of this polarization may be either

left-handed or right-handed and depends on the particular material. Right-circularly polarized light scattered from a right-handed cholesteric liquid crystal will remain right-circularly polarized but left-hand circularly polarized light impinged on the same material will be transmitted without a change in sense and will not be scattered. That is, cholesteric materials have a property similar to circular dichroism (the selective absorption of right or left-hand polarized light) except that there is no appreciable absorption of polarized light of either sense.

It can be deduced from the optical properties that the ordering in the cholesteric phase is a bulk property and not merely a surface effect. Since these substances are liquids it can further be concluded that the optical effects must arise from very weak intermolecular forces. This is the key to the application of the optical properties to non-destructive testing. Because of the weak intermolecular forces the structure and therefore the optical properties are very sensitive to changes in the environment such as temperature, rate of shear, pressure, applied electric or magnetic fields and absorption of chemicals from the ambient atmosphere.

Another important factor which must be kept in mind when considering the utilization of the color changes of cholesteric liquid crystals is that the wavelength of maximum scattering is a function not only of the angle of incidence of the light but also a function of the viewing angle of the scattered light. This angular dependence must be well understood for the proper application of a given liquid crystal. Changing the temperature or the environment of the system will cause the wavelength for maximum scattering to shift from ultraviolet to infrared. The reason for this change is a change in pitch of the characteristic helix of the structure. As might also be expected, the particular color changes to be expected from a given substance also depend in a very complicated manner on the molecular structure of the compound. Some empirical rules relating structure to color sensitivity have been formulated. For example, derivatives of cholesterol with long side chains exhibit a high sensitivity of color to temperature changes, whereas those with short chains show low temperature sensitivity. Intermediate temperature sensitivity can be obtained by using mixtures of short

and long chain compounds. The technique of formulating and using the correct mixture is a highly developed art.

If the absolute temperature of a process is required, cholesteric liquid crystals can still be used provided that the proper calibration can be performed. Several techniques have been developed to accomplish such calibrations. Perhaps the most obvious technique is to hold the temperature of the system constant and measure the reflectance at several points by means of a spectrophotometer. The disadvantages of this method are the high cost of the necessary equipment and the great amount of time needed to perform a calibration. Simpler and less expensive methods have been developed and are described in Reference 2.

The response time of cholesteric liquid crystals is finite and comparatively large because the process by which a visible color change occurs is a two-step process. An instantaneous change in the temperature of a cholesteric liquid crystal causes it to assume a new pitch. However, this requires that some material flows to a different configuration. The rate at which such flow occurs is limited by the viscosity of the material in the direction of flow. The time constant for ordinary cholesteric materials is on the order of 0.1 sec. For example, for cholesteryl nonanoate it is 0.1 sec and for cholesteryl oleyl carbonate it is 0.2 sec. These response times do not indicate a limitation if the materials are to be observed by the eye. Motion pictures at 64 frames per second have been made successfully and information determined from single frames.

Applications

As discussed in the preceding paragraphs, cholesteric liquid crystals have optical properties that are very sensitive to changes in their environment such as temperature changes, pressure changes and absorption of chemicals. In the following sections specific applications of these properties will be discussed. In some cases general procedures or sets of principles will be given which can serve as useful guides to anyone attempting to apply liquid crystal techniques to his non-destructive testing problems.

The particular advantages of liquid crystal methods for thermal mapping will be discussed under the sections on particular applications. In general, the advantages over other methods are low cost, higher sensitivity, higher resolution, simplicity and speed. There are some disadvantages and limitations. Perhaps the most obvious is the rather low temperature at which they can be used. In air, the limit is about 190 C and in the absence of air, 270 C². Moreover, the high temperature materials crystallize and tend to separate from solution at room temperature thereby complicating their application. Another disadvantage is the short lifetime of liquid crystals due to chemical decomposition when exposed to air, especially at elevated temperatures. At room temperature three to four hours is about the limit. However, methods of encapsulating the material have been developed and these overcome the problem. In the National Cash Register process the material is encapsulated in spheres approximately 50 microns in diameter. This encapsulated material can be used in the same manner as the pure material in many applications. The two chief disadvantages--the slight loss in resolution and increase in heat capacity per unit area because of the need to use thicker films--are usually not serious enough to prevent use of the encapsulated material where long-term stability is required for a particular test procedure.

Thermal Mapping. If it is desired to use the temperature-dependent color changes of cholesteric liquid crystals in a particular system, several conditions must be met if there is to be any hope for success. A set of six such conditions is given in Reference 2. These can be summarized as follows:

1. The heat capacity of the object to be studied should be larger than the heat capacity of the cholesteric film. Since the heat capacity of most cholesteric liquid crystals is on the order of 1.5 joules/cm³ and sheets of about 0.02 mm in thickness are usually used, the heat capacity per square centimeter is about 3×10^{-3} joules/cm². Unless the test specimen is a very thin film, this is sufficiently low.

2. The specimen to be examined must be larger than the resolution of the liquid crystal. This is usually about 0.02 mm.
3. The rate of temperature change in the system being examined must be sufficiently slow for the liquid crystal to follow. That is, the relaxation time must be no less than about 0.1 sec.
4. The temperature range of the specimen during the test must be in the range covered by available liquid crystals. For most purposes this means a temperature range of 0 to 75 C, although special materials have been applied successfully above 100 C for testing semiconductor devices.
5. The surface to which the liquid crystal is to be applied must be oil-resistant or made so by coating with an oil-insoluble film such as polyvinyl alcohol.
6. The surface must be black or made black by application of a black dye.

Before attempting to apply cholesteric liquid crystals for thermal mapping of a given specimen it is necessary to determine which operating parameters or material characteristics contribute to the thermal distribution to be examined. The pattern will usually indicate the intensity of power dissipation or the thermal conductivity at various points in the specimen.

Application to Electronic Devices. In this application a current flow is used to generate a temperature pattern by dissipation of power. This method has been of very great use in locating defects in electronic solid state components which very often cannot be detected by any other method. Reliable tests have already been developed for integrated circuits, silicon rectifiers, heating elements, thin-film capacitors and other electronic devices. A typical example is the detection of hot spots in silicon rectifiers³. Liquid crystalline material was painted on the device and current passing through it increased until breakdown was observed on the oscilloscope

monitor. The problem area was indicated quite clearly by the change in color of the liquid crystal layer at the points of breakdown.

Liquid crystal methods are particularly advantageous for testing integrated circuits, in which fragility and high component density prohibits the use of probe devices. Another advantage is simplicity; all that is needed, besides the liquid crystals, are a microscope and a good source of illumination. The technique has been highly developed at IBM's Component Division at Fishkill⁴, New York, where it has become a regularly used tool in quality control and design. Thermal mapping is useful not only in detecting hot spots and malfunctioning components, but also in assisting designers in distributing the power equally about the device.

Application to Testing of Materials. Thermal patterns may also be generated by differences in thermal conductivity of a specimen. By means of liquid crystal techniques very good results have been obtained in detecting and locating voids, cracks and imperfect bonds in many kinds of systems. Typical is the detection of bad bonds in steel honeycomb structures. This is accomplished by placing the specimen to be examined on a block of ice after coating the top surface with a cholesteric liquid crystal operating in the 24 to 25 C range and then gently blowing hot air over the top surface. The well-bonded areas conducted heat away at a faster rate from the warm upper surface to the cold lower surface than the poorly bonded areas. The poorly bonded areas showed up as blue and the well bonded areas became red. Liquid crystal techniques have also been applied to detecting faulty bonds in fiberglass structures³.

The advantages of liquid crystal methods over other techniques are many. Most obvious is the low cost. No expensive and elaborate equipment is needed; all that is required are a few bottles of material, a means of applying it to the specimen and a means of applying heat or extracting it from the specimen. Very often no other way of thermal mapping is available. It is not possible to use thermocouples since one would require about one million per square inch to equal the resolution of liquid crystal.

Medical Applications. Cholesteric liquid crystals have also been used in thermal mapping of human skin both for basic studies of the circulatory system and for diagnosis of diseases of the circulatory system and detection of tumors. The basic idea is that areas of the body in which circulation is poor will have lower temperatures than areas in which circulation is good. Details of the method can be found in Reference 5. This particular application is somewhat outside the scope of this report and will not be discussed further.

Infrared and Microwave Detection. The thermally induced color changes in cholesteric systems have also found application in the detection and mapping of low frequency radiation fields. Typical of this application is the work of Hansen, Fergason and Okaya, who used it to observe various far-field node patterns of a He-Ne 3.3μ gas laser beam.⁶ To accomplish this a detector was made by coating a radiation-absorbing layer with a liquid crystal which in turn is covered with a transparent membrane. The detector is held at the proper operating temperature by controlling the radiation that is allowed to fall on the detector. The beam is impinged on the opaque side of the detector and local heating proportional to the radiation density results. The resulting temperature pattern is then observed by reflected light from a mercury arc lamp. A similar detector was used to obtain two-dimensional interferograms by use of a 10.6μ CO_2 laser. Microencapsulated liquid crystals were used and kept at the proper operating temperature by means of radiation from a hot wire.⁷

Liquid crystal detectors have also been developed for the mapping of microwave radiation. Radiation modes and standing waves set between an antenna and a reflector have been observed.⁸ An interesting possible application here is the development of a microwave fluoroscope. This device would consist of an X band power source capable of providing several watts to a divider. The two branches of the divider would feed into two collimating antennas about a foot apart. Plane standing waves would be created between the antennas. The color of a liquid crystal detecting device placed between the antennas would depend on its location. If the detector were placed in a trough of the wave pattern, then a minimum amount of energy would be absorbed

and the color observed would be that corresponding to the minimum temperature. If the detector were then moved from trough to peak its color would change but would always remain uniform as long as it was kept perpendicular to the plane of the radiation. If a sheet of uniform dielectric material were inserted into the cavity then a phase shift would occur and the detector would change color but still have a uniform color. However, if a non-uniform specimen were inserted in the gap, differences in loss or phase would occur and show up on the detector screen as color contours. Once the method is perfected, it should have wide application to the detection of flaws, cracks and imperfections in dielectric materials.

Applications of Mechanically-Induced Color Changes. As discussed earlier, color changes may also be caused in cholesteric systems by application of mechanical stress. Few applications have been made of this phenomenon in comparison with applications of thermally induced color change, because the color response is much less pronounced. In the future, however, one can expect much wider exploitation of the phenomenon as more is learned about liquid crystal mixtures.

Measurement of Skin Friction in Wind Tunnel Models. In this application, liquid crystals having low sensitivity to temperature changes are used to measure local skin friction of small scale wind tunnel models by observation of color patterns induced by variations in stress caused by the air passing by the model. A liquid crystal mixture having low temperature sensitivity but high shear sensitivity is necessary for this application. Typical mixtures that meet these criteria are discussed in Reference 9. Apparatus for the calibration of the mixtures used in these experiments has been developed. In this apparatus shear forces are measured directly at the same time as peak spectral intensity of the light scattered is measured.¹⁰

Color Changes Induced by Absorption of Chemical Vapors. The absorption of vapors of many chemicals also can cause color changes in cholesteric liquid crystals similar to those caused by temperature variations.

The mechanism for these changes is probably the alteration of the rather weak structure of the liquid crystal by the foreign molecules, which can cause a change in optical properties. The sensitivity is such that only a few parts per million can be detected.¹¹

Problems and Required Research

Although many fundamental physical aspects of color changes are not well understood, enough is known to make use of these color changes in practical application. In thermal mapping applications there is little fundamental research that is badly needed at present. The principles and techniques here are all very well known. However, the application of these is not always straightforward and often requires the advice and even the physical assistance of an expert with years of experience in the field.

In microwave detection by liquid crystals further work is needed on the development of the microwave fluoroscope discussed earlier. Problems in the calibration and development of the hardware remain to be solved.

The extension of the application of the color responses induced mechanically requires more fundamental work of the type described in References 9 and 10. That is, basic studies of the spectral response to pressure should be made for many different materials and a theory should be developed to correlate the data.

A very large amount of work is needed on the effect of absorption of vapors on the colors exhibited by cholesteric liquid crystals. The fact that the sensitivity of these substances is very high would seem to indicate that they would be very useful wherever small amounts of poisonous vapors would be likely to be present as in space vehicles, mines, garages, etc. However, there has never been a systematic study of this effect and as a result practical applications have lagged. Good studies of some aspects of the phenomenon have been made¹¹ but there has never been a concerted attack on understanding the fundamental phenomena.

2. Liquid Crystals in Display Devices

Fundamental Principles

All of the liquid crystal display devices so far conceived make use of the effect of electric fields on nematic and cholesteric materials. Electric fields affect the behavior of a liquid crystal in two conflicting ways.¹² First, an electric field tends to align all the molecules of a nematic system so that the dipole moments are all pointing in the same direction. In general this is to be expected. However, there are exceptions in which the molecular structure is such that the alignment is the result of conduction. (See Reference 99 of Part II) Since the dipole moment in general does not have to lie along the major axis of the molecule, the molecules in an electric field need not be aligned parallel to the field but rather parallel to each other at an angle to the field. Some molecules may even line up perpendicularly to an electric field because their electric dipole moment is perpendicular to the long axis of the molecule. Nematic solutions contain ions, either from impurities or from dissociation of some of the nematic molecules themselves. When an electric field is applied, the ions present in the system move and disturb the regular array of nematic molecules. Large regions of turbulence are thus created. These turbulent regions scatter light isotropically causing the nematic liquid crystal to appear milky white. This effect is called dynamic scattering¹³. This phenomenon can be stopped and the transparency of the liquid crystal restored by turning off the applied field. When this is done the turbulence ceases since the ions cease their motion and the molecules become locally ordered again under the influence of their mutual van der Waals forces. The important point here is that a thin film of a nematic liquid crystal is clear, in the absence of an electric field even though the ordering is only local.

Another way in which moving ions can be utilized is called the storage mode¹⁴. This phenomenon occurs in mixtures of nematic substances that exhibit dynamic scattering and cholesteric substances. Such mixtures are fairly clear and also become milky white when a direct current or low

frequency electric field is applied. Furthermore, the system remains white even after the field is turned off and regains its clarity only after several weeks. However, an alternating field of frequency greater than 4000 Hz and strength greater than about 3×10^4 V/cm will quickly restore transparency. A possible mechanism for this clearing is that moving ions create large regions of turbulence as in the dynamic scattering mode. The turbulence also causes emulsification of the two components of the mixture and so when the field is removed the molecules of the nematic material are unable to become ordered. When an alternating electric field of sufficient strength is applied, the molecules line up so that their dipole moments are parallel to the field. If the field is of sufficiently high frequency the ions cannot move sufficiently far to cause turbulence but merely oscillate in place about an equilibrium position.

As was implied above, if the dipole moment of a molecule of a nematic material is in the same direction as the major axis, ions can pass through the system without setting up much turbulence and very little light is scattered. Such materials would seem to be useless for display devices. However, they can be used in conjunction with dichroic dyes to produce color effects.¹² Dichroic dyes absorb plane-polarized light only when they are oriented at the proper angle with respect to the plane of polarization. An example of a useful mixture of a nematic liquid crystal and a dichroic dye is indophenol blue in p-ethoxybenzylidene-p'-aminobenzonitrile, the color of which is a vivid blue. If polarized light is passed through this system while there is a voltage across it, the blue color disappears and the material becomes clear. The blue color comes back when the voltage is removed. The explanation of the phenomenon is that when the voltage is applied the nematic molecules line up with the field and force the dye molecules to line up with the field also. If the parameters of the system have been selected properly, then the resulting orientation of the dye molecules is away from the proper angle for blue light absorption and the result is no color. Removal of the field allows the dye molecules to assume a random orientation. Therefore, some of the molecules will be at the proper angle and absorption will be

able to occur. The use of nematic liquid crystals as matrices for dichroic dyes has been named the "host-guest" mode.¹²

Application to Devices

The first consideration in designing a liquid crystal display device is the proper selection of the nematic material to be used. This must be in the nematic phase over the entire temperature range over which the device is to be used. For ordinary consumer applications such as television screens, a substance that is nematic from about 10 C to 35 C would be adequate. For certain specialized military or aerospace applications such a substance might not be adequate because of greater temperature ranges encountered. The discovery and preparation of nematic materials is in general still a problem and much research is being devoted to it. One approach is to use eutectic mixtures of two or more high-temperature nematics. However, such mixtures have the disadvantage of crystallizing with time and use because of the presence of impurities and because of temperature cycling. Ideally, only single component, non-crystallizing nematics should be considered for device applications.¹⁶

Once the proper nematic material is available, the construction of a simple display device is fairly easy. All that is required besides the nematic liquid crystal is two glass plates coated on one side with a conducting material. Tin oxide, which is transparent as well as electrically conducting, is a good material for this purpose, since at least one of the glass plates must be transparent for viewing by reflected light. Both plates must be transparent if the device is to be used to control transmitted rather than reflected light. For reflecting light devices the rear plate can be coated with aluminum. The conducting material which serves as the electrodes is formed in the pattern to be displayed for permanently displayed material such as in advertising or street signs. For other applications such as instrument readout and television screens, the coating is applied as a regular array of patches to each of which voltage can be applied independently. By applying voltage to the proper set of patches the desired information or picture can be displayed.

Problems and Required Research

In principle all of the knowledge and techniques needed for the construction of practical display devices utilizing liquid crystals are available. However, there are still obstacles to the practical realization of these principles in a commercial device. One of these is the lifetime of the liquid crystal used in the device. Many nematic and cholesteric substances which would otherwise be very suitable for display devices are sensitive to temperature and ultraviolet light and decompose after a few hours. The synthesis of new liquid crystals for display devices and their testing for lifetime represents a very large part of the liquid crystal research being done in industrial laboratories today. As one would imagine, the results of these investigations are highly proprietary. However, some laboratories have claimed to have beaten the lifetime problem and claim to be able to make storage mode devices capable of being used for several thousand hours. The results for dynamic scattering devices are said to be almost as good. Another set of problems that must be solved deals with the development of methods of scanning and the associated electronic circuitry. For television and radar display screens it is obviously not practical to construct the screen out of a grid of many small patches of conducting material, each one of which would be an electrode. About 25,000 such electrodes would be needed to equal the resolution of a standard television set. Electron beam scanning has been tried successfully but is not the final answer, since one still needs a vacuum for the method to work and the resulting display device would be just about as bulky as a standard cathode ray tube.

Because of their many advantages--flat construction, reflective or transmissive mode of operation, high contrast ratio, low power requirements, and high resolution--the development of liquid crystal devices is a very worthwhile activity despite the obstacles described above. In the very near future simple display devices, such as clock faces and instrument readouts, will be available.

3. Liquid Crystals as Research Tools

Of relatively little commercial and technological importance but of very high actual and potential scientific importance is the growing number of applications of liquid crystals in fundamental research. Examples of important laboratory applications are the use of liquid crystals as solvents for nuclear magnetic resonance studies of molecular structure, solvents for chemical reactions and as chromatographic media. In general, wherever an ordering matrix or medium in an experimental investigation is needed liquid crystals may be considered. In the following sections many of the laboratory uses of liquid crystals will be discussed. Where appropriate, possible future applications to technological problems will be mentioned.

Solvents in Magnetic Resonance

In a previous section of this report there was presented a rather thorough discussion of the use of magnetic resonance techniques in studying ordering in liquid crystals. In this section the use of liquid crystals as solvents for the study of the structure of small molecules by means of NMR, a technique that was introduced by Englert and Saupe in 1963¹⁷, is covered. Although the technique has become widely used, only a brief discussion will be given here since many reviews of the subject are available¹⁸⁻²².

In the usual high resolution NMR experiments the molecule to be studied is dissolved in an ordinary isotropic liquid. In such liquids the molecules are free to move translationally and rotationally. As a result of the free orientation only the average values of the shift and coupling parameters can be observed. This simplifies the interpretation of the resulting spectrum enormously but simultaneously leads to much loss of information about the structure of the molecule being observed. However, in a liquid crystal medium some of the rotational degrees of freedom are lost and much information not obtainable from NMR work in isotropic liquids can be retrieved. Specifically the direct nuclear dipole interactions, from which it is possible

to deduce the geometry of the molecule, are obtained. The method cannot give the absolute size of a molecule but it can give ratios of interatomic distances and values of interbond angles, with accuracy very comparable to other methods of structure determination. The accuracy is limited chiefly by how well molecular vibrations can be taken into consideration in interpreting the spectra. In many cases the amplitudes of the various modes and their degrees of anharmonicity are not known. Another limitation is the complexity of the spectra. So far, difficulties in interpretation of the spectra have limited the technique to small organic molecules containing eight or fewer protons. Using deuterium substitution may make the method applicable to more complex molecules.

Another type of magnetic resonance, electron spin resonance, (ESR), may also be carried out on molecules dissolved in liquid crystal solvents. These measurements are much easier to perform than NMR measurements, because the ESR transitions are more intense and because the homogeneity of the magnetic field is not important. However, the method is limited to the study of radicals that are stable in liquid crystal solvents. ESR studies in liquid crystals have been of use mostly in determining the degree of order in nematic systems.

Solvents for Chemical Reactions

A new and rather exciting possibility is the use of liquid crystals as media for chemical reactions, in particular organic reactions in which stereospecificity is a factor in determining the path of a particular reaction and its kinetics. The basic concept is that the stereospecificity is promoted by solvents in which the molecules are oriented parallel along their long axes. Very little work has been reported in the literature so far. A typical example of what has been done is the work of Bacon and Brown²³ on the Claisen rearrangement. The rate of the Claisen rearrangement of allyl *p*-tolyl ether in a nematic liquid was found to be comparable to the rate found in some proton donating solvents. Since the nematic solvent used in this work does

not donate protons to increase the rate of reaction, the increased rate is concluded to be due to the stereoselective character of the nematic solvent. Further studies of this reaction as well as studies of polymerization of phenyl acetylene are being conducted at Kent State University.

Other important work has been done in the USSR.²⁴ Typical examples are studies of some polymerization reactions. In one of these studies a mixture of 0.5 mole of p -H₂C:CMeCO₂C₆H₄CO₂H (I) and 1.0 mole of p Me(CH₂)₁₅OC₆H₄CO₂H (II) were found to form a smectic liquid crystalline mixture between 83 C and 134 C. Polymerization of (I) was induced by addition of (tert-Bu)₂O₂. The rate of polymerization was found to be much greater in the smectic phase than in the liquid phase. The average molecular weight of the polymer was 6×10^5 in contrast to the molecular weight of 6×10^4 obtained by polymerization in HCONMe₂. Significant differences were found for the intrinsic viscosities of polymers formed in the liquid crystalline phase and those formed in the liquid phase. The results were explainable on the basis of the alignment of molecules of (I) within smectic layers.

Chromatography by Use of Liquid Crystals

Closely related to the idea of using liquid crystals as solvents for stereospecific reactions is the use of such substances as media for chromatographic separation of difficult to separate compounds. Since this topic has already been covered in some detail earlier, only a brief discussion will be given here for the sake of completeness. Liquid crystals should be good for this application by selectively discriminating on the basis of molecular shape. These expectations have been fulfilled in practice. For example, the positional isomers of disubstituted benzenes have been separated by means of gas-liquid chromatography (glpc)²⁵. It was found that in the separation of meta and para isomers that the para isomer was preferentially dissolved and retained by the liquid crystal. The use of glpc as a tool for the purification of organic reagents appears to be very promising and much work has been done on this type of application. Another possible use is in the study of how the various molecular characteristics contribute to

the stability of liquid crystalline phases and in exploring the solvent properties of liquid crystals. By doing glpc studies one may be able to determine the relative importance of packing factors and length to breadth ratio in the stability of liquid crystalline phases. Beginnings in this area of study have been made.²⁵

B. FUTURE APPLICATIONS

In previous sections applications of the properties of liquid crystals that have already been conceived have been discussed. Even if there were no other possible applications, much research and development would be needed merely to perfect and expand the scope of the techniques and devices already known. However, there are many more possibilities--properties yet to be applied and extension of laboratory techniques to technology, for example. In the following sections some of the possible future exploitations of liquid crystals will be discussed and evaluated. In some cases ideas that have been proven to be unsound will also be mentioned in order to assist the reader interested in particular applications to avoid pitfalls.

1. Properties for Future Exploitation

As discussed earlier in this report, some of the unusual properties of liquid crystals have been thoroughly exploited. Most prominent among these are the various applications of the optical properties in non-destructive testing and the combined application of optical properties and response to electric fields for display devices. However, there are many properties of liquid crystals that have not been combined in useful ways yet. The number of possibilities in combining the unusual properties of liquid crystals described in the state-of-the-art sections of this report is limited only by the imagination of the reader. Some examples of possible properties that can be exploited after more research has been performed are outlined below.

Ordering Properties

By ordering properties we mean the ability of a liquid crystal to influence the spatial arrangement of substances dissolved in it. In previous sections well-established applications of these properties such as in nuclear magnetic resonance, electron paramagnetic resonance and chromatography have been discussed. In this section some unproven and rather speculative applications will be taken up.

Liquid Crystals as Media for Cross-linkage of Polymer Chains.

Recently, de Gennes has suggested the possibility of using liquid crystals as solvents for the formation of cross-linked polymers of unusual properties, both optical and mechanical.²⁶ The nature of the particular polymer would depend on the particular type of liquid crystal used as a medium. For example, in nematic systems the dissolved polymer chains are stretched out along the direction of the director $\underline{n}(r)$ of the solvent. If cross-linkage is induced there is formed a cross-linked polymer network extending in that direction. However, on extraction of the liquid crystal solvent, this network would relax into an isotropic, three-dimensional network of great strength. In the case of a smectic liquid crystal dissolved polymer chains occupy the space in between layers of solvent. Inducing cross-linking would result only in the linking together of chains sandwiched between the same two layers. Washing out the liquid crystal solvent would leave a substance consisting of a stack of platelets each of which is only one molecule thick. Each of these plates would be very strong but the binding between them would be very weak much like the case of graphite. Such a substance would have very unusual mechanical properties and may perhaps be useful as a solid lubricant. In cholesterics the preferred direction $\underline{n}(r)$ varies from point to point and describes a spiral (See Part II). As in nematic solvents, polymer chains dissolved are aligned along the direction of $\underline{n}(r)$. When cross-linkage is induced a twisted netted structure is obtained. On rinsing away the solvent such a twisted structure is not able to relax but holds its shape. That is, the resulting polymer would have spiral symmetry and would have high optical rotatory power.

The reader at this point should be cautioned that the above ideas are still very speculative and have yet to be demonstrated as being feasible in the laboratory. No one has yet, to the authors' knowledge, succeeded in carrying out any of the above-mentioned cross-linkages in a liquid crystal solvent. In principle, however, there is no reason why they should not be feasible. There are fairly obvious difficulties to be overcome. Even if a polymer having the proper cross-linking possibilities is found, a suitable liquid crystal solvent must be found in which the polymer is sufficiently soluble and whose viscosity is low enough to allow the orientation of the system, either by electric field or magnetic field. Another possible difficulty is the initiation of the cross-linking reaction, since really high temperatures cannot be used with liquid crystals. However, radiation or some catalyst may be found to overcome the difficulty in particular cases. None of the above difficulties appears insuperable and it is not unreasonable to expect that in the not too distant future these difficulties will be overcome and some materials of unusual optical and mechanical properties will be prepared by cross-polymerization in oriented solvents.

Rheological Properties

The viscosity and flow characteristics of liquid crystals and the effect of external influences on these have been discussed earlier in this report (Section II D). As was pointed out there, our knowledge of the rheological properties of liquid crystals is meager. The reason for this is the difficulty of making reproducible and accurate measurements because of the great sensitivity of the measurements to the conditions of the surface over which the material is flowing. Because of this and because of the strong possibility that impure liquid crystals were used, much of the early research on the effects of electric and magnetic fields on viscosity cannot be relied upon. However, the measurements do show, at least qualitatively, that large effects can be present.

At present no application is being made of the field effects on viscosity of liquid crystals. Until much more research is carried out in

a carefully controlled manner with highly purified liquid crystals, it is probably that no practical use of the unique rheological properties will be made.

Magneto-Optical Properties and Electro-Optical Properties

In previous sections we have already discussed many of the applications that have been made of the effects of electric fields on the optical properties of liquid crystalline systems. In Part II many effects involving magnetic fields were discussed such as the untwisting of cholesteric helices by magnetic fields, the alignment of nematics by magnetic fields and the effect of magnetic and electrical field on light-scattering properties. In this section the possibilities of applying some of these effects will be discussed.

In Section B of Part II, the change of pitch of cholesteric helices by magnetic fields was discussed. The light scattering properties of cholesteric materials are very sensitive to pitch. An obvious application then is to use a cholesteric liquid crystal as a magnetic field mapping device. Such a device would consist of a thin sheet of a cholesteric material, either pure or mixed, held between two transparent plates, a light source and a means for detecting the scattered light (in most cases visual observation would suffice). Such a device would be very useful only in applications where strong magnetic fields (several thousand Gauss) must be measured, such as particle accelerators and magnetic resonance apparatus. The practical realization of liquid crystals in magnetic field strength measurement depends on the formulation of cholesteric material having sufficient sensitivity. Also, a method of calibrating the device must be devised. If this can be accomplished it will be possible to map magnetic fields merely by putting the device in the field and observing the distribution of the colors present.

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13. ABSTRACT

Liquid crystals are true liquids which have surface tension and the ability to flow and yet have some of optical properties of crystals. Though these materials have been known for over eighty years, interest has been rekindled over the last ten years because of their many interesting technological applications. Modern research tools have provided much new basic information about the structure and properties of these materials. This basic information has been used to solve many technological problems and develop new devices. In classic fashion the successful application of known properties of liquid crystals has stimulated further basic research in the expectation of further practical exploitation of these unusual materials. Use of liquid crystals has been made in a wide variety of areas ranging from nondestructive testing by thermal mapping to display devices. Future applications of present day basic research will probably lie in the rheological properties, ordering properties and magneto-optical and electro-optical properties.

The present report is a brief state-of-the-art survey aimed at bringing the reader up to date on what is known of the fundamental properties of liquid crystals and their applications - potential as well as actual. The report is divided into three parts: a historical survey of the development of the science of liquid crystals, a summary of present knowledge of the physical and chemical properties of liquid crystals, and a section on present and possible future applications. Theories of the structure of liquid crystals, thermodynamics, the effect of external forces and fields, viscosity and diffusion, optical properties, and many other physical topics are discussed. Also covered in some detail are the correlation of molecular structure with liquid crystallinity, a synthesis of liquid crystals, and polymorphism.

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